BUSINESS & PUBLICATION OFFICES
20TH AND NORTHAMPTON STREETS
EASTON, PENNSYLVANIA

EDITORIAL OFFICE
KENT CHEMICAL LABORATORY
THE UNIVERSITY OF CHICAGO

OTTO REINMUTH, *Editor*

VIRGINIA GORE, *Assistant to the Editor*
HARVEY F. MACK, *Business Manager*
CYRUS S. FLECK, *Assistant Business Manager*
B. F. GOULD, *Advertising Manager*
C. L. WELLS, *Circulation Manager*

BOARD OF PUBLICATION
T. L. DAVIS
G. J. ESSELEN
H. N. HOLMES
O. M. SMITH
N. W. RAKESTRAW

DEPARTMENTAL EDITORS
H. C. SHERMAN, *Graduate*
W. SEGERBLOM, *High School*
TENNEY L. DAVIS, *Historical*
R. E. ROSE, *Industrial*
M. M. HARING, *Undergraduate*

CONTRIBUTING EDITORS

G. A. ABBOTT
B. H. BALL
A. P. BLACK
W. E. BRADT
G. H. BRANDES
C. A. BRAUTLECHT
J. M. BRECKENRIDGE
B. S. BRONSON
F. E. BROWN
H. W. BRUBAKER
C. A. BUEHLER
T. F. BUEHRER
H. A. CARPENTER
F. E. CLARK
J. D. CLARK
A. J. CURRIER
F. B. DAINS
L. C. DAVY
N. DIETZ, JR.
Q. C. DRAKE
A. L. ELDER
W. G. EVERSOLE
O. R. FOSTER
J. H. GRAHAM
G. C. GREENWOOD
J. S. GUY
W. A. HAMMOND
E. B. HARTSHORN
C. A. HASKEW
C. C. HEDGES
G. B. HEISIG
B. C. HENDRICKS
H. N. HOLMES
B. S. HOPKINS
J. W. HOWARD
S. F. HOWARD
S. W. HOYT
J. B. LUCAS
E. G. MAHIN
R. N. MAXSON
R. K. MCALPINE
W. MCCRORY
A. E. MCKINNEY
J. P. MONTGOMERY
H. W. MOSELEY
L. ONCLEY
A. M. PARDEE
J. L. PARSONS
L. E. PORTER
F. H. PRITTIE
E. L. QUINN
G. R. ROBERTSON
W. F. RUDD
H. SCHLUNDT
G. W. SEARS
O. F. STAFFORD
R. E. SWAIN
A. P. SY
R. B. THOMPSON
T. G. THOMPSON
R. G. TURNER
W. A. VAN WINKLE
B. A. VOIT
G. H. WHITEFORD
G. Y. WILLIAMS
L. F. WILLIAMS

FOREIGN EDITORS

F. LAMBERMONT, *Belgium*
W. LASH MILLER, *Canada*
F. G. DONNAN, *England*
ATHERTON SEIDELL, *France*
K. FREUDENBERG, *Germany*
ERNST COHEN, *Holland*
N. PARRAVANO, *Italy*
WOJCIECH SWIETOSLAWSKI, *Poland*
ST. MINOVICI, *Roumania*
SIR JAMES IRVINE, *Scotland*
E. MOLES, *Spain*
W. D. TREADWELL, *Switzerland*
H. RHEINBOLDT, *Brazil*

Entered as second-class matter, January 31, 1924, at the Post Office at Easton, Pa., under the act of March 3, 1879. Accepted for mailing at special rate of postage provided for in Section 1103, Act of October 3, 1917, authorized January 31, 1924.

COPYRIGHT, 1938, BY DIVISION OF CHEMICAL EDUCATION, AMERICAN CHEMICAL SOCIETY

The JOURNAL OF CHEMICAL EDUCATION *is indexed in the Education Index, Industrial Arts Index, and, in part, in the Quarterly Cumulative Index Medicus*

JOURNAL OF CHEMICAL EDUCATION

for February, 1938

OFFICIAL MONTHLY PUBLICATION OF THE
DIVISION OF CHEMICAL EDUCATION OF THE
AMERICAN CHEMICAL SOCIETY

B. C. HENDRICKS, *Chairman*
N. W. RAKESTRAW, *Secretary*
M. V. MCGILL, *Vice-Chairman*
VIRGINIA BARTOW, *Treasurer*

Volume 15, Number 2 Contains

FRONTISPIECE—FRIEDRICH KONRAD BEILSTEIN 51

EDITOR'S OUTLOOK 52

JANE MARCET AND HER "CONVERSATIONS ON CHEMISTRY" 53
Eva V. Armstrong

A HISTORY OF EARLY ANTISEPTICS 58
Melvin F. W. Dunker

THE INSPIRATIONAL ELEMENT IN THE TEACHING OF CHEMISTRY 61
M. L. Crossley

CHEMISTRY AND THE POEMS OF ERASMUS DARWIN 63
George W. Eckert

A RÉSUMÉ OF ELECTRON DIFFRACTION 64
G. L. Clark and E. Wolthuis

ON THE WRITING OF CHEMICAL EQUATIONS 75
Albert L. Jacobs

THE METAL CARBONYLS. V AND VI 77
Wm. E. Trout, Jr.

A NEW DISTILLATION COLUMN 83
E. H. Parke

RESEARCH PROBLEMS FOR SECONDARY SCHOOL PUPILS 84
Verne R. Ross

AN IODOMETRIC METHOD FOR THE ESTIMATION OF SILVER 86
Claude K. Deischer and Wallace M. McNabb

THE ELIZABETH CLAY HOWALD SCHOLARSHIP 87

AN EXPERIMENT ON HETEROGENEOUS EQUILIBRIUM 88
Arthur A. Vernon

A CYCLIC REACTION SCHEME ILLUSTRATING CARBOHYDRATE METABOLISM 89
V. R. Potter and C. A. Elvehjem

SOME PRACTICAL HELPS IN ORGANIC ANALYSIS 92
G. H. Cheesman

A NEW AND INEXPENSIVE SODIUM PRESS 93
E. H. Parke

ABSTRACTS 94

RECENT BOOKS 97

TRADE ANNOUNCEMENTS XII

Subscription Price: $3.00 per year; Canada $3.50; other countries $4.00. Single copies of issues in current year, 50c each; all other single copies, one dollar. Foreign remittances must be accompanied by International Money Order. Issued monthly.

No claims for copies of journals lost in the mails can be allowed unless such claims are received within sixty (60) days of the date of issue and no claims can be allowed for issues lost as a result of insufficient notice of change of address.

Manuscript for publication should be directed to the editor or to one of the departmental or contributing editors. Prospective authors are urged to avoid diffuse writing and to observe the forms outlined in our Notice to Authors of Papers as it appears on page 671 of the December, 1934, issue.

IF IT IS CHEMICALLY FEASIBLE

Baker & Adamson will produce *to order* any inorganic compound, of any desired purity, with any specified set of compatible physical properties.

Those whose unusual needs may not be covered in our catalog of 1000 C.P. Acids and Reagent Grade Chemicals will find B & A production-to-order an efficient branch of a chemical service animated by the principle: *It can be done.*

FOR EXAMPLE:

Manganous Oxide. Until recently, obtainable only through import. B & A is now producing it to order, to exacting specifications.

Calcium Acetate, purified. "Custom-made" by B & A, in quantity lots, to unusual specifications regarding purity, solubility and physical make-up.

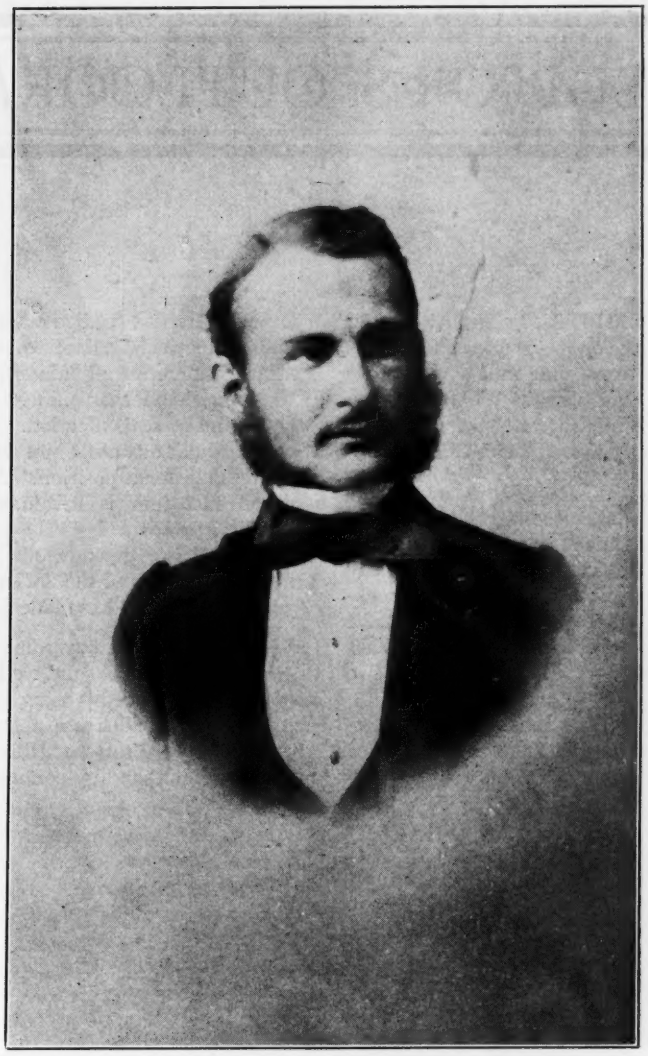
SETTING THE PACE IN CHEMICAL PURITY SINCE 1882

BAKER & ADAMSON

Reagent Chemicals AND *C.P. Acids*

Division of GENERAL CHEMICAL COMPANY, 40 Rector St., New York

Atlanta • Baltimore • Boston • Buffalo • Charlotte • Chicago • Cleveland • Denver • Kansas City • Los Angeles • Minneapolis • Philadelphia • Pittsburgh • Providence • San Francisco • St. Louis



FRIEDRICH KONRAD BEILSTEIN
(1838–1906)

THE centennial anniversary of his birth will this month be observed by organic chemists throughout the world because of his establishment of the monumental reference directory to the literature of organic compounds, which still bears his name. During the last twenty-five years of Beilstein's life this work passed under his personal supervision through three editions of ever-increasing size; now, just one hundred years after his birth, the fourth edition, with its superb systematic classification devised by Paul Jacobsen, is completing, in fifty-four magnificent volumes, its treatment of the knowledge of organic compounds of definite structure.

Beilstein was born of German parents in St. Petersburg. Beginning his chemical education at the age of fifteen under Bunsen at Heidelberg, he subsequently worked in the laboratories of Liebig (Munich), Wöhler (Göttingen), Wurtz (Paris), and Loewig (Breslau). He became an intimate friend of Kekulé, Fittig, and Hübner and with them shared in the editing of the *Zeitschrift für Chemie*. In 1866 he was called to succeed Mendeléeff at the Imperial Technological Institute of St. Petersburg, and except for travel never again left the land of his birth. Although at first continuing in Russia the experimental investigations which had made him well known, he ultimately forsook all research for the development of the beloved "Handbuch' which he had first started at Göttingen. The first edition (two volumes of 2201 pages) appeared in 1880–1882, the second (three volumes of 4080 pages) between 1886–1890, and the third (four volumes of 6844 pages) between 1892–1899. With the assistance of the German Chemical Society this was extended by a supplement (five volumes of 4604 pages) between 1899–1906 so that Beilstein himself lived to see the completion of the third edition. The present fourth edition whose publication was commenced by the German Chemical Society in 1918 already comprises fifty-four volumes of some 30,000 pages and some additional material (dealing with natural products of undetermined structure) still remains to be printed.

(*Dr. Ernest H. Huntress of Massachusetts Institute of Technology contributed the biographical sketch presented here.*

Dr. E. Berl of Carnegie Institute of Technology lent the photograph here reproduced.)

BOSTON UNIVERSITY
COLLEGE OF LIBERAL ARTS
LIBRARY

EDITOR'S OUTLOOK

A CAREER IN CHEMISTRY. The two brief contributions by E. H. Parke on pages 83 and 93 of this number were transmitted to us some time ago by Contributing Editor Harry N. Holmes. We felt at the time—and still feel—that many readers would enjoy sharing Professor Holmes's transmitting letter with us. He wrote in part as follows.

"Mr. Parke is not a college graduate but he is an intelligent man who has made a career for himself out of this position. He has been with me nearly twenty-two years in Oberlin in charge of our stockroom, of the janitor, and as purchasing agent. I have encouraged him to be inventive, and he has been, with good results, as you see from these two articles.

"Mr. Parke took a correspondence course in business in order to improve himself, and he has worked at the typewriter until he can write his own business letters. He has studied the students and interested himself in their welfare to such a point that I am afraid our returning alumni are more anxious to shake his hand than mine. Many of these alumni hold him in real affection. Furthermore, I find it worth while to consult him whenever I recommend a young man for a position. As you see, such an all-round factotum is invaluable—a member of the family.

"Mr. Parke attends our seminars and goes to nearby meetings of the Society. I commend him to you as a man who has made a career."

We hope that we may some day have the pleasure of meeting Mr. Parke, and we have no wish to embarrass him in advance by using Professor Holmes's little pen vignette to illustrate a homily. Probably, after all, the facts, as Professor Holmes has given them, are more eloquent than any commentary of ours could be.

HOW CAN INDUSTRY GET AND HOLD COMPETENT TECHNICIANS? Some time ago we called attention in these columns to *Chemical Industries*' then-current symposium on "Why Chemists Get Fired," which dealt with the commoner deficiencies of the young industrial chemist or chemical engineer as his employer sees them. Some of the defects cited were such that they could be corrected only by self-education. Others were made the basis of suggestions for modifications in the content or methods of university instruction.

Something of the other side of the problem of training chemists and chemical engineers for industry is presented in the sequel symposium under the above title. In it fourteen university contributors discuss the personnel policies of industry, and suggest means whereby the industry may aid the universities and their faculties in improving the training of technical personnel. We believe that our readers will find the second symposium as interesting and instructive as the first. Incidentally, Mr. Haynes has written us that a collective reprint of both symposia is now available. (Chemical Industries, 149 Temple Street, New Haven, Conn., $0.10 each, 25 for $1.00, 100 for $2.50.)

JANE MARCET *and* HER "CONVERSATIONS *on* CHEMISTRY"*

EVA V. ARMSTRONG

The Edgar Fahs Smith Memorial Collection in the History of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania

IN 1769 the first independent chair in chemistry in the American Colonies was established at the University of Pennsylvania, the occupant being Benjamin Rush, a student of Joseph Black. Prior to this date, chemistry was taught here under the heading of natural philosophy, unaccompanied by experimental demonstrations. It was conceded to be desirable as a part of the education of a gentleman, but the interest of the general public in the subject was negligible. So far as the man in the street was concerned, the only use he had for a chemist was to supply pharmaceutical remedies when home treatment and simples failed. The knowledge that chemistry could contribute materially to his comfort and welfare, or provide a basis for a vast industrial development such as the world had never witnessed, was completely lacking.

In the same year, 1769, seven years before the birth of our country as a nation, a "blessed event" occurred in a Swiss family of comfortable circumstances, living in London. The child was baptized Jane, with the family name of Haldimand. She was welcomed and endowed with loving care. One could not expect too much of a girl child, and there was no seer to prophesy that fate would cross her path with some of the greatest personalities of the period, that she would become intimately acquainted with men eminent in political economy, philosophy, and chemistry; and that through a clear and delightful interpretation of some of their achievements as set forth in her "Conversations on Chemistry," she would contribute, in no small degree, to a popular knowledge and understanding of chemistry in England and in France; no one dreamed that in a republic yet unborn thousands of copies of her book would be perused, willingly or unwillingly, by thousands of young democrats, to the end that a popular appreciation of the subject should be there instilled: or that, finally, a young man named Michael Faraday, binding her book in an obscure shop in London, should be inspired by its contents to dedicate himself to a science in which his name became immortal.

Jane's life was divided between residence in London and frequent visits to relatives in Geneva. She was a literal-minded child, and de la Rive relates an incident which occurred when she was eight years of age. She heard her grandmother complain that her watch was running badly and, in a fit of exasperation, say that she would gladly be rid of it for a guinea. The next day Jane came to her grandmother and proudly gave her a guinea and a half, explaining that she had disposed of the watch to a clock-maker at what she considered a good bargain. The poor child expected to be praised, but it was a reprimand that she received. "My dear child," said the old woman, a little sharply, "it is not always necessary to take all that one says literally."

JANE MARCET, 1769–1858

But no more at eight than at eighty could Jane understand how anyone could say one thing and mean another.

Jane was barely fifteen when she lost her mother and found herself the head of a large household. She discharged the duties of a mother toward her brothers and sister, and between her father and herself there grew up

* Presented before the Division of History of Chemistry at the ninety-fourth meeting of the A. C. S., Rochester, New York, September 6, 1937.

BOSTON UNIVERSITY
COLLEGE OF LIBERAL ARTS
LIBRARY

a close and rare companionship which lasted until his death. A visit to Italy with him when she was seventeen contributed to the development of a talent for painting. As hostess in her father's home she met men eminent in the arts, and thus became a friend and pupil of the celebrated Reynolds and of Thomas Lawrence.

In 1799 Jane Haldimand married Alexander Marcet, a native of Geneva, who held an appointment as physician at Guy's Hospital, London, which he later relinquished to devote himself exclusively to experimental chemistry. He was the author of several scientific papers. As the wife of an eminent physician and chemist, Mrs. Marcet found herself a member of a distinguished literary and scientific circle. Here she met

ALEXANDER MARCET, 1770–1822
SWISS PHYSICIAN AND CHEMIST LECTURED ON CHEMISTRY AT GUY'S HOSPITAL, LONDON. CONTRIBUTED TO THE FIELD OF PHYSIOLOGICAL CHEMISTRY

Lord Brougham, Jeffrey, and Sydney Smith, founders of the *Edinburgh Review;* Hallam, the historian; the political economists Malthus, Rossi of Italy, and Harriet Martineau; Maria Edgeworth, English novelist; the naturalist, Candolle; Auguste de la Rive, Wollaston, and many others. According to de la Rive, one of the chief characteristics of Jane Marcet was a genuine thirst for knowledge. She had, in addition, intelligence, personality, and charm. She attended the lectures of Sir Humphry Davy and others, and later met the distinguished scientists at evening gatherings. As Desdemona to these Othellos of science, she listened wide-eyed to the stories of their discoveries. Flattered and intrigued by so attentive a listener, they were doubtless led to discuss fluently the subjects so dear to their hearts. Her husband encouraged her interest, and additional explanation of details was available to her through his contacts and his knowledge of chemistry. Before his death in 1822 he had the satisfaction of seeing her established as a successful author of popular books on science.

In 1805, Jane Marcet published anonymously her first book "Conversations on Chemistry," in which the elements of that science are familiarly explained and illustrated by experiment. In an informal dialogue between Mrs. Bryan, the teacher, and Emily and Caroline, the pupils, she set forth the discoveries of Galvani, Volta, Franklin, Count Rumford, Priestley, Oersted, Berzelius, Berthollet, Cavendish, Lavoisier, Black, Wollaston, Davy, and other masters of the art.

In the preface to this book she states,

> "In venturing to offer to the public . . . an Introduction to Chemistry, the author . . . a woman, conceives that some explanation may be required; and she feels it the more necessary to apologize for the present undertaking as her knowledge of the subject is but recent, and as she can have no real claims to the title of chemist."

Mrs. Marcet was especially qualified to write for the young. She understood their attitude of mind, she aroused their interest and curiosity and encouraged them to ask questions. She had a delightful style, vivacious and clear. She had a passion for truth and never sacrificed a fact for an effect. She allowed her imagination full play in the method of presentation, but in content she followed only the truth as she knew it. She dramatized great discoveries in chemistry, and it is impossible to read a chapter of her book without coming to believe that Mrs. Bryan and Emily and Caroline are real personalities, that Mrs. Bryan is performing the experiments which she describes so vividly, to the interest and amazement of Emily and Caroline, that she is actually using the apparatus pictured in the woodcuts in the book, and answering the questions of her pupils. It may be said that Mrs. Marcet's most important contribution to chemistry was her advocacy of the teaching of chemistry to beginners by experimental demonstration, in a day when the value of this was not fully recognized.

Constantly alert for new facts in chemistry, Mrs. Marcet revised and corrected later editions. In the fifth London edition, 1817, she states that she has

> "endeavoured to give an account of the principal discoveries which have been made within the last four years in Chemical Science . . . and of various important applications, such as gas-lights, and the miner's lamp. . ."

A portion of the dialogue on gas-lights follows.

Caroline: Mrs. B.—in those beautiful lights, called gas-lights, which are now to be seen in so many streets . . . I can perceive no wick at all. How are these lights managed?

Mrs. Bryan: In this mode of lighting the gas is conveyed to the extremity of a tube, where it is kindled and burns as long as the supply continues. There is, therefore, no occasion for a wick. . .

Emily: But how is this gas produced in such large quantities?

Mrs. Bryan: It is obtained from coal, by distillation. . .

Emily: What an admirable contrivance. Do you not think, Mrs. B.—that it will soon be universally adopted?

Mrs. Bryan: Most probably; for the purpose of lighting streets, offices, and public places, for it far surpasses any former invention; but in regard to the interior of private houses, this mode of lighting has not yet been sufficiently tried to know whether it will be found generally desirable, either with respect to economy or convenience. It may, however, be considered as one of the happiest applications of chemistry to the comforts of life. . .

In the eighth London edition, the author introduced the "late discoveries on Electro-Magnetism, and the doctrine of Definite Proportions."

Mrs. Marcet was not pedantic in her teaching; she was refreshingly natural and unaffected, and when Caroline, impressed by the word "oxydate" in Mrs. Bryan's talk on oxidation, proposes to use it thereafter, exclaiming, "Rust is a word that should be exploded in chemistry," Mrs. Marcet warns her to

> ". . . take care not to introduce the word oxydate in general conversation; for you would probably not be understood, and you might be suspected of affectation."

Mrs. Marcet had a keen appreciation of the work of Sir Humphry Davy, and referred to his researches on potassium and sodium in the following dialogue.

Mrs. Bryan: Before we part, I must introduce to your acquaintance the curious metals which Sir Humphry Davy has recently discovered. The history of these extraordinary bodies is yet so much in its infancy that I shall confine myself to a very short account of them; it is more important to point out to you the vast, and apparently inexhaustible, field of research which has been thrown open to our view by Sir Humphry Davy's memorable discoveries, than to enter into a minute account of particular bodies or experiments.

Caroline: But I have heard that these discoveries, however splendid and extraordinary, are not very likely to prove of any great benefit to the world, as they are rather objects of curiosity than of use.

Mrs. Bryan: Such may be the illiberal conclusions of the ignorant and narrow minded; but those who can duly estimate the advantages of enlarging the sphere of science, must be convinced that the acquisition of every new fact, however unconnected it may at first appear with practical utility, must ultimately prove beneficial to mankind.

Caroline: What a satisfaction Sir Humphry Davy must have felt, when by an effort of genius he succeeded in bringing to light, and actually giving existence to these curious bodies, which without him might perhaps have ever remained concealed from our view.

Mrs. Marcet's prompt adoption of Sir Humphry Davy's theories and discoveries was criticized rather harshly by some of her contemporaries, particularly by the editors of American editions of her work. Thomas Cooper, who edited an edition in 1818, concurred in the criticism, but expressed his opinion more gallantly than some of his colleagues. He wrote,

". . . The late discoveries in Chemistry having changed the face of the whole Science, have rendered a new edition of Conversations on Chemistry absolutely necessary . . . which the authoress published in two volumes in July 1817. In this publication, she has explained, and implicitly adopted all Sir Humphry Davy's discoveries and opinions; even when his other contemporaries in chemical investigation, have not yet dared to follow him. This renders the book extremely interesting, as presenting theoretical views of the subject not to be met with in the modern compilations; but at the same time, it renders explanations necessary, lest the young student should adopt as certainties, many theoretical views, which have hardly yet arrived at probability. I have therefore thought it worth while to insert a few notes and illustrations, to show more accurately than Mrs. Bryan has done, the actual state of the chemical facts, and the present value of the chemical theories she has adopted, that the reader may tread with caution paths not yet fully explored. . . This is a very elegant and useful compilation; I have endeavoured to contribute nothing to its elegance, but something to its usefulness."

That Mrs. Marcet disarmed her critics by a cheerful and ready acceptance of their judgment is shown by a statement included in the 1813 edition of her book,

> "The author is not aware of having omitted to notice any new essential improvement or discovery in Chemical Philosophy; but she feels no difficulty in acknowledging that she has been rather more cautious, than she was on former occasions, in adopting doctrines or theories which have not received the sanction of time, or the approbation of more enlightened judges."

Her continued endeavor to include new discoveries in chemistry in her book is shown in a letter which she wrote to Michael Faraday on November 24, 1845. She was then in her seventy-first year.

> "Dear Mr. Faraday, I have this morning read in the "Athenaeum," some account of a discovery you announce . . . respecting the identity of the imponderable agents, heat, light, and electricity; and as I am at this moment correcting the sheets of my "Conversations on Chemistry" for a new edition, might I take the liberty of begging you to inform me where I could obtain a current account of this discovery? It is, I fear, of too abstruse a nature to be adapted to my young pupils; yet I cannot make up my mind to publish a new edition without making mention of it; I have, therefore, kept back the proof sheets of the Conversation on Electricity which I was this morning revising, until I receive your answer, in hopes of being able to introduce it in that sheet."

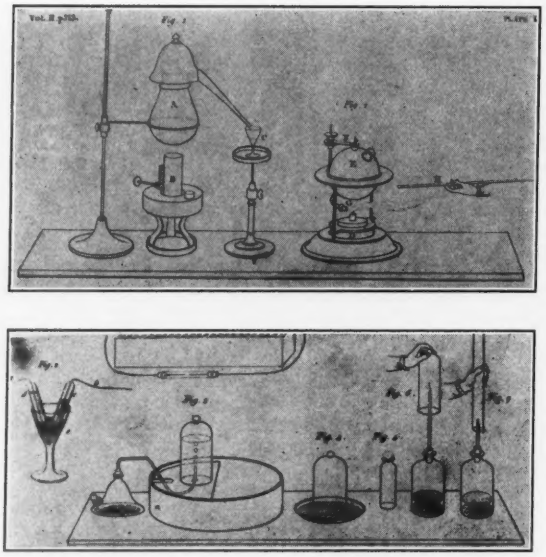
The closing paragraphs of Mrs. Marcet's "Conversations on Chemistry" are of interest.

> "Art contrives the sphere of useful purpose, to which the elements were intended by nature, and the production of the several kingdoms are frequently arrested in their course, and variously modified, by human skill, which compels them to contribute, under new forms, to the necessities and luxuries of man.
>
> "But all that we enjoy, whether produced by the spontaneous operation of nature, or the ingenious efforts of art, proceed alike from the goodness of Providence. To God alone man owes the admirable faculties which enable him to improve and modify the productions of nature, no less than these productions themselves. In contemplating the works of the creation, or studying the inventions of art, let us therefore, never forget the Divine Source from which they proceed; and thus every acquisition of knowledge will prove a lesson of piety and virtue."

Mrs. Marcet's friendship with Maria Edgeworth began with an incident connected with "Conversations on Chemistry." A younger sister of Miss Edgeworth accidentally swallowed a poisonous acid which placed her life in danger. At the time, she was far

removed from medical aid. No one knew what to do, when suddenly a statement in "Conversations on Chemistry" was recalled, to the effect that an alkali such as magnesia would serve to neutralize certain acids. The prescription was immediately followed, and the young girl's life was saved. Maria Edgeworth addressed a letter of gratitude to the anonymous author of "Conversations on Chemistry," and some years later the two women met in London and became fast friends.

Sixteen editions of Mrs. Marcet's "Conversations on Chemistry" were published in England, most of them anonymously, although the London edition of 1846 bears her name on the title-page. Two French translations and fifteen American editions have come to the notice of the author of this paper. There were doubtless others. Fourteen editions have found sanctuary in the Edgar Fahs Smith Memorial Collection of the University of Pennsylvania.



ILLUSTRATIONS OF APPARATUS FROM "CONVERSATIONS ON CHEMISTRY" BY JANE MARCET, LONDON, 1817. DRAWN BY THE AUTHOR AND ENGRAVED BY LOWRY

One hundred and sixty thousand copies of the book were sold in the United States prior to 1853. The American editors noted are Professor William H. Keating of the University of Pennsylvania, Thomas Cooper, and John Lee Comstock, M.D., of Connecticut, assisted in one edition by the Reverend J. L. Blake. An edition of the book was published at Greenfield, Massachusetts, by an anonymous editor who called himself "An American Gentleman." In 1831 Thomas P. Jones, professor of chemistry in the medical department of Columbian College, Washington City, issued "New Conversations on Chemistry, founded on Mrs. Marcet's Conversations on Chemistry." This is the only American edition noted with Mrs. Marcet's name on the title page; in the other editions, the editors omit any mention of Mrs. Marcet or refer to her in the preface as "Mrs. Bryan." In "New Conversations on Chemistry" Thomas P. Jones took Mrs. Bryan, Caroline, and Emily over bodily, using some of the original dialogue and substituting much of his own as an improvement. In other American editions the editors used the original dialogue, and contented themselves by inserting footnotes containing supplementary material.

In addition to "Conversations on Chemistry," Mrs. Marcet wrote "Conversations on Political Economy," which brought her considerable fame. It was highly praised by Lord Macauley and Jean-Baptiste Say. McCulloch, writing in 1845, pronounced it "the best introduction to the science that has yet appeared." This was followed by "Conversations on Natural Philosophy" and by "Conversations on Vegetable Physiology," the latter work being inspired by Mrs. Marcet's close association with Candolle. In addition she wrote a number of books for little children, which were classics in their day.

Mrs. Marcet passed away in London at the age of eighty-nine years. The finest tribute to her memory was penned by Michael Faraday in a letter to Auguste de la Rive.

"Your subject interested me deeply in every way, for Mrs. Marcet was a good friend to me, as she must have been to many of the human race. I entered the shop of a bookseller and bookbinder at the age of 13, in the year 1804, remained there eight years, and during the chief part of the time bound books. Now it was in those books, in the hours after work, that I found the beginning of my philosophy. There were two that especially helped me, the "Encyclopædia Britannica," from which I gained my first notions of electricity, and Mrs. Marcet's "Conversations on Chemistry" which gave me my foundation in that science.

"Do not suppose that I was a very deep thinker, or was marked as a precocious person. I was a very lively, imaginative person, and could believe in the "Arabian Nights" as easily as in the "Encyclopædia," but facts were important to me, and saved me. I could trust a fact, and always cross-examined an assertion. So when I questioned Mrs. Marcet's little book by such experiments as I could find means to perform, and found it true to the facts as I could understand them, I felt that I had got hold of an anchor in chemical knowledge, and clung fast to it. Hence my deep veneration for Mrs. Marcet; first, as one who had conferred great personal good and pleasure on me, and then as one able to convey the truth and principle of those boundless fields of knowledge which concern natural things, to the young, untaught, and inquiring mind.

"You may imagine my delight when I came to know Mrs. Marcet personally; how often I cast my thoughts backwards, delighting to connect the past and the present; how often, when sending a paper to her as a thank-offering, I thought of my first instructress, and such like thoughts will remain with me."

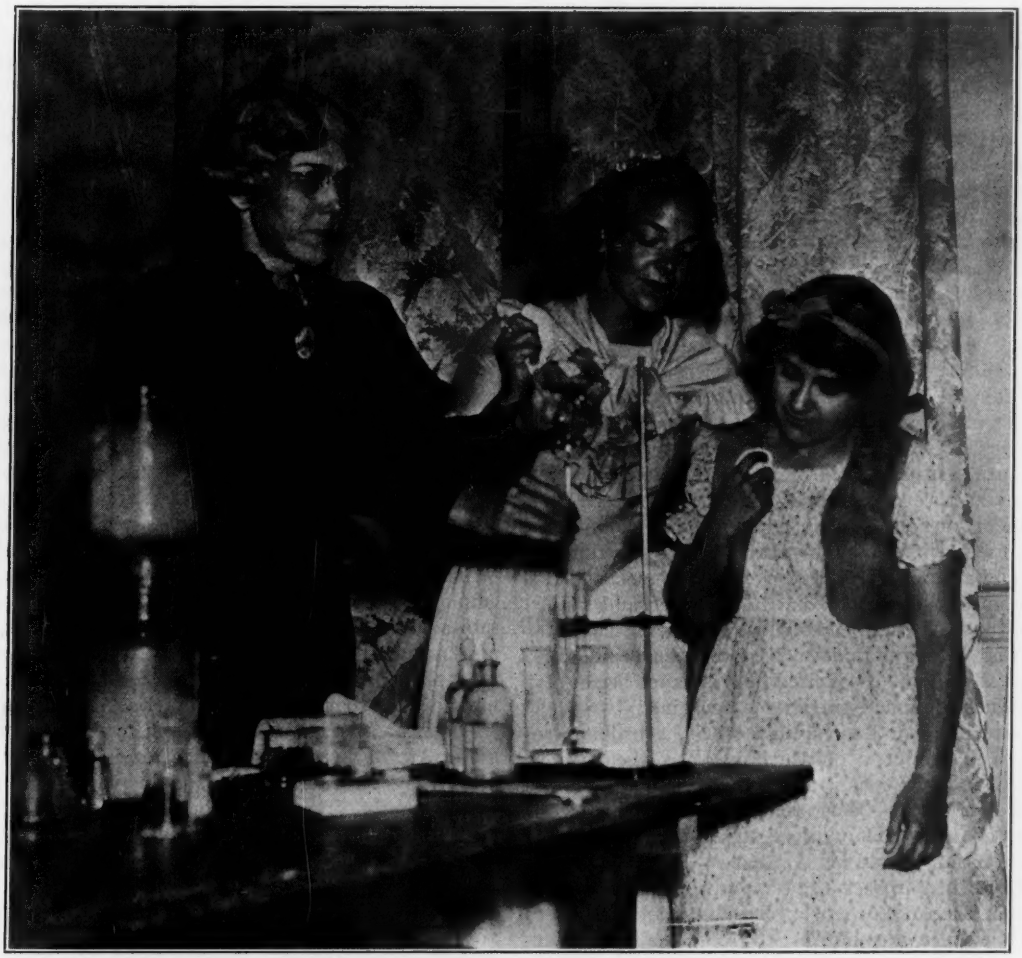
ACKNOWLEDGMENT

The author is indebted to Mr. Ralph A. Copeland, B.S. in Chemistry, 1937, University of Pennsylvania,

for a translation of de la Rive's article on Madame Marcet. Valuable assistance was also rendered by Miss Josephine Cook, reference assistant of the University of Pennsylvania Library.

LITERATURE CONSULTED

"Conversations on Chemistry," by Jane Marcet. Various editions, **1806–1846.**
"Biographical Sketches," by Harriet Martineau. New York City, **1869.**
"Harriet Martineau's Autobiography." Boston, **1877.**
"Life and Letters of Faraday," by Bence Jones. London, **1870.**
"Women's Record," by Sarah J. Hale. New York City, **1870.**
"Madame Marcet," by Auguste de la Rive. In Bibliothèque Revue Suisse et Étrangère. LXIV^me^ Année, Nouvelle Période. Tome Quatrième, Genève, **1859,** pp. 445–68.
American Monthly Magazine, **1,** 387 (1833).
Gentlemen's Magazine, **2,** 204 (1858).



Courtesy of Democrat-Chronicle, Rochester, New York

"CONVERSATIONS ON CHEMISTRY": LEFT TO RIGHT, MRS. BRYAN, EMILY, CAROLINE

Following the presentation at Rochester before the History Division of Miss Armstrong's paper on "Jane Marcet and Her 'Conversations on Chemistry'," Mrs. Bryan, Emily and Caroline dramatized, in costume and with experiments, Conversation XIX. "On the . . . . Muriatic and Oxygenated Muriatic Acids; and on Muriats." The sixth English edition, 1819, was used for the script. Caroline, the curious and unbelieving pupil, was interpreted by Anna Bianchi and Emily, the reasoning and diligent one, by Hilda H. Torstensen, both girls of the graduate school in chemistry at Ohio State University. Mildred W. Grafflin of the Hercules Experiment Station, Wilmington, Delaware, took the part of Mrs. Bryan, the teacher.

A HISTORY *of* EARLY ANTISEPTICS*

MELVIN F. W. DUNKER

University of Maryland, Baltimore, Maryland

SOME medical historians are wont to divide surgical history into two periods, "Before Lister" and "After Lister." In this period "After Lister" we are accustomed to take for granted the germ theory of disease and the limitless benefits of antiseptic methods. Such, however, was not always the case. It is only within the past three-quarters of a century that the causal relationship of microörganisms to disease has been definitely and irrefutably established and that truly antiseptic methods of surgery have been established.

"Before Lister" a hospital was by no means the safest place in which to have an operation of even minor character performed, and the larger the hospital, the less the chances for surviving. Records from the "Before Lister" period reveal that following amputations of the arm, forearm, thigh, or leg the mortality from postoperative infection in England was forty-one per cent. in the large hospitals and eleven per cent. in country practice. In the large Parisian hospitals the mortality rate in similar instances was as high as sixty-two per cent. The death rate from wound infections in field hospitals was even greater. Sir Charles Bell, a professor of surgery at Edinburgh during the first quarter of the nineteenth century, gives the following picture of hospitals: you look "upon limbs variously wounded, but all of them lying out, swollen, suppurating, fistulous, rotting in their own filth, having carious bones, bleeding arteries and a profusion of matter; the patient exhausted in the meanwhile, with diarrhoea, fever and pain." Wrench in his "Life of Lord Lister" makes the statement that during periods such as wars and epidemics, a hospital could be recognized at a distance because of "the stench of human putridity it contained."

All are more or less familiar with the brilliant researches of Pasteur, upon which are based the development of post-Listerian antiseptic surgery and the tremendous progress since that time. Perhaps a conception of the notions of infection, sepsis, and antisepsis "Before Lister" would be of value.

For present purposes, the term antiseptic will be employed in a broad sense, to apply to any method used to check the effect or counteract the influence of the agencies which produce sepsis or to destroy them in both living and non-living matter. The methods may be divided into two large classes—the physical and the chemical. Some chemical materials have been used because of their physical effects in altering osmotic pressure. Certain salts produced their effect by desiccation rather than through any specific ion action.

The early attempts at what we call antisepsis were applied chiefly to the preservation of foods. The process of desiccation is one of the oldest. As early examples of this, we have the dried flesh found in the Egyptian mummies and the hay and dried fruits found in tombs, the smoking and drying of meat, and the drying of fish. In other cases the desiccation has been brought about by making use of the osmotic pressure developed; *e. g.*, from time immemorial, meat and fish have been kept by pickling or salting, and fruits have been conserved with honey or sugar.

Within rather recent times ultra-violet light has been advocated for the rapid sterilization of certain types of materials and solutions. Ultra-violet light, although not known as such, was recommended more than twenty-five centuries ago, for in the Sanskrit writing "Susruta Samluta" of about 800 B.C. we read, "It is good to keep water in copper vessels and to expose it to sunlight and and to filter through charcoal."

It is quite certain that heat has long been recognized as a means of preventing bacterial decomposition, but definite references to its very early use seem to be lacking. In the seventh century A.D., Paul d'Égine recommended the treatment of abscesses with heat, while in the tenth century, Albucasis practised the actual cauterization of abscesses. Cauterization was also later employed in amputations. The standard treatment for rabies in humans was the cauterization of all teeth marks with a red hot iron. In the eighteenth century an Italian priest by the name of Spallanzani was the first to show that heat killed bacteria. About the year 1800, there appeared a monograph by Appert entitled "The Art of Preserving Animal and Vegetable Substances." The method consisted in placing the material in tightly corked or stoppered bottles and exposing these to the temperature of boiling water. Shortly after the beginning of the nineteenth century, Danson and Symington recommended exposing the articles of clothing worn by sick people to rapid currents of air heated to a temperature varying from 200° to 250°F. In 1831, Dr. Henry of Manchester advised the sterilization of clothing by heating it in a copper vessel surrounded by steam.

A public health measure which may be regarded as a physical means of retarding the spread of infection is indicated by the attention which the Greeks and the Romans gave to crowding in urban localities; they enacted laws governing the proper construction of houses,

* Presented before the Division of Medicinal Chemistry at the ninety-third meeting of the A. C. S., Chapel Hill, North Carolina, April 13, 1937.

specifying varying distances between them according to size. The elaborate sewage systems developed, especially by the Romans, are matters of historical record. Moses, in the early Biblical writings, established specific hygienic rules for camps and cities and described with great care the modes of disinfecting vessels, clothing, and houses contaminated with putrid or infectious matter. In the twelfth and thirteenth chapters of Leviticus, he described the symptoms of leprosy and directed the segregation of lepers.

Proper ventilation, as a hygienic measure, is comparatively new; its value to homes and ships was not realized until the eighteenth century. About the same period various gases, as the oxides of nitrogen, chlorine, nitric acid vapors and so on, were advocated for fumigating sick rooms.

The sterilization of solutions by ultrafiltration represents a comparatively modern advance.

Chemicals which we now recognize as antiseptics were, in the early days, generally used for preservative purposes as the mixtures in which they occurred naturally as, for instance, tar, resins, gums, and the like. While the art of fermentation was known thousands of years before the Christian era, the fact that putrefaction is just another form of fermentation was not appreciated. Egyptian embalming is an example of the effort to resist putrefaction. The brain and viscera were removed and the body preserved with spices and aromatics to await unchanged the "summons to the Elysian fields of Aahlu." Even before the time of recorded history, such substances as resins, pitch, bitumen, aromatics, nitre, and cedar oil were used by the Egyptians for this purpose. The use of aromatics was eventually extended to the preservation of foods. Turpentine from *Pistacia terebinthus* (not the common turpentine of today) was added to wine in Palestine and myrrh was used by the Romans to prevent the souring of wine. Bitter herbs were used from the start and owed their virtues in preventing change partly to their tannin which coagulated albuminous substances, and partly to essential oils and alkaloids which acted as the antiseptics. Among those used were mugwort (*Artemisia bulgaris*), alecost (*Chrysanthemum balsamita*), alehoof (*Nepeta glechoma*), wormwood (*Artemisia absynthium*), chamomile, quassia, gentian, hop, and pepper.

Man's instinctive repugnance to offensive odors early taught him to mask their presence. The ancients employed perfumes and substances with decided odors regularly as guards against infection and contagion. From the days of Homer and Hippocrates, the burning of sulfur and tar has been practised for the arrest of pestilence. At Hippocrates' time, sulfur was regarded as an antidote against plague. Ovid makes mention of the fact that sulfur was used by the shepherds of his time for bleaching fleeces and for purifying their wool from contagious diseases. Today we realize that the value of these substances lay in their antiseptic properties.

In contrast to our modern idea, let us consider for a while the pseudo-antisepsis of the ancients as proposed by Hippocrates about 460 B.C. Knowing nothing of the cause of infection, Hippocrates applied to wounds substances which are now recognized as antiseptics. However, the instruments and dressings employed were themselves never sterilized or protected from contamination. These attempts can hardly be considered truly antiseptic. On the other hand, an examination of ancient writings assembled by Galen (born 130 A.D.) leads Anagnostakis (1889) to insist that Hippocrates was the originator of the idea of antiseptic treatment. This author asserts that in the surgery of Hippocrates, the drying of the wounds constitutes the antisepsis and the drying agents are accordingly the antiseptics. His argument is: if you succeed in drying a wound according to the method of the ancients, have you not accomplished the same purpose as by killing the bacteria by modern methods? Hippocrates recommended an ointment of tar (the original source of carbolic acid) for the treatment of wound surfaces. It was one of Hippocrates' ideas that fresh wounds, except those of the abdomen, should be allowed to bleed for some time, to prevent the inflammation of the wound and the surrounding tissues. The logic behind this was that any infection pressed into the wound was washed out. He employed bandages and poultices of various cooling mixtures of plants, of flour paste, and a warm linseed cataplasm not directly in the wound, but after it had been dried. It was naturally necessary to re-dress the wound often. He also gave directions for preparing agglutinating and antiputrefying plasters with resins and asphalt. According to Anagnostakis, the complete wound treatment of Hippocrates was as follows.

1. After stopping the hemorrhage, wash the area with warm wine; in eye injuries use a weak salt solution.
2. Wipe dry with a linen cloth.
3. Anoint the wound surfaces with tar or with a solution of a copper salt mixed with aromatics and bitters.
4. Reunite the borders of the wound (suture).
5. Dust with antiseptic powders such as copper salts, aromatics, resins.
6. Cover the area with a tar plaster.
7. Coat the surrounding parts with a cerate to prevent the entrance of air.
8. Apply compresses soaked in wine.
9. Cover the entire area with a linen bandage.

After Hippocrates, there followed a period during which nothing of interest in antiseptics is found until we come to Celsus in the first century A.D. He described the activity and strength of the drugs known to him, and included under styptics, the drugs affecting suppuration. He described various wounds, the morphology of blood and pus and the treatment of wounds according to two principles: (1) care for stopping the hemorrhage and (2) reduction of the inflammation. The wound was packed with dry linen, compressed, and moistened with a "liniment" of vinegar. For some severe cases, he recommended cauterization with a red hot iron.

In the second century A.D., Dioscorides is supposed to have called sea salt an antiseptic. He used it on recent

wounds, sometimes as a powder and sometimes as a solution. After an operation, he put a little powdered salt in the wound. Various copper salts were highly recommended by Oribasus in the third century A.D. for preserving moist surfaces. Copper acetate was regarded as a drying agent and slow detergent.

Theodore Bourgogni, whose work represents a great improvement, described a means of sewing wounds shut and then covering them with light compresses of warm wine. He disapproved of putting any foreign matter into the wound as it only hindered healing, and he believed that suppuration represented a destruction of the course of healing and was to be avoided.

In the thirteenth century Rogerius protested against the use of gauze which interfered with the natural operations of repair. He used only wine and honey on wound surfaces. Bruno instituted the practice of closing all incised wounds at once, appreciating the beneficial effect of granulation.

The fifteenth century supplied little of value in the field of antiseptics. During the sixteenth century some definite progress was made, namely: the reassertion of the part played by nature as the principal agent in healing, the relinquishment of the idea that physicians had had the power to make flesh or tissue, and the abandonment of the idea that wounds may be fed. The first declaration that air was infectious was made in this century.

The seventeenth century marked the dawn of what may be called the modern history of antiseptics. It was in this century that the compound microscope was developed by Leeuwenhoek, and in 1675 he first observed microörganisms.

Sir John Colbatch in 1698 recommended the use of dilute sulfurous acid solution internally to combat malignant fever. He also claimed to have prepared a powder for dressing wounds which gave wonderful results in healing, although he did not divulge his formula.

The eighteenth century produced no very highly significant discoveries along antiseptic lines. However, it was in this period that Sir John Pringle made what was probably the first crude attempt at comparing the relative bacteriostatic activity of various salts and drugs. He concluded that the acids as well as the alkaline salts were among the most powerful antiseptics. He rated the comparative powers of the salts in resisting putrefaction as follows, using salt as a standard: sea salt, 1; rock salt, 1; potassium sulfate, 2; ammonium acetate, 2; potassium acetate, 2; ammonium chloride, 3; salt of wormwood, 4; potassium nitrate, 4; ammonium carbonate, 4; borax, 12; salt of amber, 20; and alum, 30. He also experimented with myrrh, aloes, asafoetida, terra japonica, gum ammoniac, opium and camphor, and found camphor to be the strongest "resister to putrefaction". Experiments with infusions of serpentaria, cinchona, pepper, ginger, saffron, contraerva root, galls, dried sage, rhubarb, wild valerian root, mint leaves, angelica, ground ivy, senna, green tea, red roses, wormwood, mustard seed, and horse-radish root proved that they were all powerful resisters of putrefaction.

The demonstration of the rapid growth of bacteria gave new support to the doctrine of "spontaneous generation," which had begun to flourish in the middle ages. In 1668, Redi began the attack on this theory and insisted that all living matter sprang from pre-existing matter. Spallanzani, about a century later, was the first to prove beyond doubt that bacteria arise by the division of their predecessors. From time to time the theory of abiogenesis was brought forth in spite of these proofs, until finally the work of Pasteur and Tyndall removed the last of the supporters of the "spontaneous generation" theory.

Notions about infective agents were many and varied. As far back as the fifth century B.C., Empedocles suggested the existence of contagia and miasma in the atmosphere. This idea was also supported by Hippocrates, as his wound treatment described earlier clearly indicated. This same idea was later shared down through the centuries by Celsus in the first century A.D., Galen in the second century, Ambrose Paré in the sixteenth century, Magatus in the seventeenth century, Pibrae, J. J. Petit, and A. Monro in the eighteenth century, and Delpech and many others including Lister in the nineteenth century. Lister, in his earlier work, feared the contamination of wounds by the atmosphere. He exercised elaborate precautions to produce an "antiseptic atmosphere," developing several types of sprays to saturate the air of the operating room with carbolic acid. Caignard de la Tour in 1836 elucidated the first step toward the establishment of the rudimentary tenets of what later developed into the germ theory of disease by finding that the dead yeast cell no longer produced fermentation. In the same year Schulze proved that putrefaction was not due to oxygen, a fact confirmed by Schwann in 1840 and by Helmholz in 1843. In 1836 Donné observed microörganisms in pus. In 1837 Beauperthius and Adet de Roseville noticed the organisms in chancrous pus and in 1838 declared them to be the cause of the infection. Schwann in a series of remarkable experiments proved the phenomena of putrefaction to be due to microörganisms. In 1850 Davainne and Rayer observed that the organisms found in the blood of animals dying of anthrax were rods. In 1861, after Pasteur's work had shown butyric acid fermentation to be caused by an organism, Davainne declared his rods to be the cause of anthrax. Schroeder and Dusch in 1854 found that filtration of air through cotton wool prevented the fermentation of sterilized broth. The recognition of the rôle of the yeast plant in alcoholic fermentation by Pasteur and others began the actual proof of the relation of microörganisms to disease. The first demonstration of the causal relationship of microörganisms to disease, a fact which had now been suspected for some time, was made by Pasteur in his work on the cause of the death of silk worms. The extensive developments in the field of bacteriology from here are quite generally known.

The foundations for the work of Lister had now been laid. Having at hand a long empirical use of coal tar and crude carbolic acid, and having at hand Pasteur's

work in bacteriology, Lister combined them all to propose his antiseptic treatment of wounds and methods of operation. It seems quite probable that without the conclusive work of Pasteur and others before him, Lister's efforts would have gone unheeded.

It should be pointed out in closing that materials and methods which were at least crudely antiseptic have been used from the beginning of written records. However, the use of these was merely empirical and entirely without the knowledge of the cause of infection or the reason for the good results sometimes obtained. For the correlation of the germ theory of disease and the deliberate use of chemicals for the antiseptic treatment of wounds, we must pass down through the ages to Lister in the nineteenth century A.D.

BIBLIOGRAPHY

ANAGNOSTAKIS, A., "La methode antiseptique chez les anciens," thesis, Athenes, **1889**, pp. 1–13.

BUCHANAN, C. M., "Antisepsis and antiseptics," The Terhune Co., Newark, New Jersey, **1895**, pp. 9, 11–23.

CUSHNY, A. R., "Pharmacology and therapeutics or the action of drugs," 6th ed., Lea and Febiger, Philadelphia, Pennsylvania, **1915**, 441.

ELLIOTT, G. F., "Ancient traces of antiseptic treatment in medicine and surgery," *Brit. Med. J.*, **1868**, II, 519.

GARRISON, F. H., "History of medicine," 4th ed., W. B. Saunders, Philadelphia, Pennsylvania, **1929**, pp. 435, 436, 577, 578, 591.

HAGGARD, H. H., "Devils, drugs and doctors," Harper & Bros., New York City, **1929**, pp. 169–75.

JONES, JOSEPH, "Progress of the discovery of disinfectants and their application for the arrest of contagion," "Medical and surgical memoirs," Vol. 3, part ii, appendix, pp. 401–95, New Orleans, Louisiana.

KAHLE, F., "Uber Antiseptik in Altertum und Mittelalter," thesis, Berlin, Hannover, **1895**, pp. 1–28.

KEEN, W. W., "Before and after Lister," *Science*, **41**, 845–53, 881–91 (1915).

DE KRUIF, PAUL, "Microbe hunters," Harcourt, Brace and Co., Inc., New York City, **1926**, pp. 3–56.

LAWALL, C. H., "Four thousand years of pharmacy," J. B. Lippincott Co., Philadelphia, Pennsylvania, **1927**, p. 584.

NOYES, R. F., "Evolution of antisepsis," *Trans. of the Rhode Island Medical Society*, **V** (1894–1898), 17–35.

PARK, ROSWELL, "An epitome of the history of medicine," 2nd ed., F. A. Davis, Philadelphia, Pennsylvania, **1899**, pp. 316–29.

RIDEAL, SAMUEL, "Disinfection and the preservation of food," 3rd ed., Sanitary Publishing Co., London, **1903**, pp. 1–6.

RIDEAL, S. AND E. RIDEAL, "Chemical disinfection and sterilization," Edward Arnold and Co., London, **1921**, pp. 1–8, 11, 12, 27, 203, 208, 225, 231, 251, 267.

ROBINSON, VICTOR, "Pathfinders in medicine," Medical Life Press, New York City, **1929**, pp. 49, 99.

SINGER, CHARLES, "A short history of medicine," Oxford University Press, New York City, **1928**, pp. 237–43.

TYREE, J. S., "The history of antiseptics" (pamphlet), n. p., 1890.

The INSPIRATIONAL ELEMENT *in the* TEACHING *of* CHEMISTRY

M. L. CROSSLEY

The Calco Chemical Company, Inc., Bound Brook, New Jersey

IN THE teaching of chemistry the essential problem is to find an effective method of presenting the organized facts of the science in thought patterns that have the greatest power of appeal in group instruction. This is a difficult task. The mass of chemical information is so great and the material is so complicated and varied as to require involved thinking to understand the simplest relationships. Besides, there are great differences in receptivity and mental capacities of the individuals in the group to be instructed. To appeal and impress, the instruction must have a quality which strikes some common human chord capable of response. Bare facts have no such common appeal. The cold facts of chemistry are seldom attractive and pleasing to the average mind. To stick, they must be charged with an inspiring quality which has the power to level the barriers of individual resistance to the acquiring of new knowledge. To be retained and digested, the facts must be accompanied by an inspirational appetizer. Flinging uninspiring information at a class is not good teaching. The method of presenting new information must be capable of stimulating the student's desire for more knowledge. His mental curiosity must be aroused before the teacher can succeed in imparting knowledge to him. The inspirational quality of his teaching should be the main concern of a good teacher.

The function of a teacher of chemistry is not that of exposing his erudite mastery of the abstract facts of the science and of demonstrating his ability to extricate himself from the bewildering mass of information bear-

ing on the question of the validity of the facts presented; it is not to serve as a "textbook spigot" from which flows a stream of chemical facts, formulas, and equations; it is to inspire men to want to know the meaning of the facts and to fire them with enthusiasm for work with a determination to succeed. All the elements that constitute the means of education must fuse into one great inspiring principle, capable of causing men to will to rise above the commonplaces of daily life in interpreting the facts of chemistry so as to enrich and ennoble mankind.

It is the significance of the facts of chemistry that lends flavor to the hash served up in the average course of instruction. The meaning of these facts in daily life and the influence of such in shaping the course of civilization, call for interpretations and evaluations beyond the range of the possibilities of the symbolic language of the science. The teaching of chemistry must light the fire of devotion to the spirit of service. It must cause men to soar to mental heights where dwell only the most sublime thoughts. It must quicken the imagination and discipline the will if it is to produce worthwhile results. It must arouse in students that element of curiosity without which human imagination, determination, and skill are but wasted talents. Besides, it must keep men marching forward enthusiastically toward the goal of high accomplishment in spite of difficulties and discouragement. Knowledge of the facts of chemistry alone has not the power to sustain interest and compel loyal devotion to the ideal of individual proficiency as a means of shaping the course of civilization. It is the inspirational element in teaching which lights the fires of enthusiasm and erects the altars of idealism for men. Teaching must be inspirational to be truly educational.

The role of the chemist is more than that of a disinterested individual who is working out a life sentence at a job provided for him by Society. He must be inspired by his training to see that his work is that of an architect of human progress. He is responsible for the designs to which social growth and economic development are builded. He is expected to understand the significance of the changes which he would bring about by the results of his investigations. In his explorations to the core of the atom or to the nucleus of a gene, he must be guided by the compass of human betterment. His course must be chosen from the best available experience charts.

These experience charts have no value in guiding the direction of human progress unless they are understood. The basis for this understanding is provided by education. The teacher is therefore privileged to see that the foundation is capable of supporting the superstructure to be erected upon it. It is not enough that men have a foundation of facts for service in chemistry. In addition, they must have capacity to evaluate the facts and interpret their significance. But interpretation involves a broad knowledge of the circumstances surrounding the facts and a sympathetic understanding of the limitations of human observation and judgments. To serve best, the chemist must be trained, then, to think beyond the facts of chemistry. He must be inspired to view his problems from the broadest possible angle embracing the most comprehensive picture of human relations. Chemistry is involved in so much of life that the chemist finds his problems to be interwoven fibers of many different strands. To unravel these strands he must be in close touch with many phases of life. He must be competent to solve the problems in chemistry and likewise capable of understanding the significance of the results obtained and the influence of these results on the course of human progress.

The inspirational element in instruction becomes the chemist's guiding star to accomplishment. What he does in life is determined by what he is prepared to see as possible of achievement. No artist paints a picture which he has not previously fashioned in his mind. He reaches out beyond the boundaries of the known and catches a glimpse of a new world which he must help to make a reality. The picture on the canvas is no greater than the artist's capacity to visualize it. We are all artists, and our creations are limited by what we are trained to expect from our efforts.

The training in chemistry must prepare men to think problems through to a satisfactory solution. This means that they must know the basic facts of chemistry and be able to relate them to the problems to be solved. The solution of any problem necessitates a definite plan. In planning the attack on a problem it is first necessary to analyze the problem to obtain its components. These have a way of being elusive. Their identification within a fair degree of certainty is often difficult and requires careful, faithful scrutiny of the facts, with a logical unprejudiced organization of convincing evidence. Being persuaded that there is a problem and knowing its nature, the next questions for consideration are its importance and the probability of finding a worthwhile solution. These considerations involve the correlation of data and the evaluation of evidence. For this, one must have, besides facts, vision. The success of the attack on a problem depends upon the excellence of the plan, the thoroughness of its execution, and the ability to recognize the significance of the results.

The ability to realize the significance of results and appreciate their importance does not come merely from an accumulation of chemical information. The process of education must do more for a chemist than to provide him with bundles of facts for storage in his mental attic. It must inspire him to examine these facts constantly and use them fearlessly in the design of the results he wishes to create or otherwise achieve. It must cultivate in him a desire to weigh the facts in his possession, in the light of new experiences, and give him courage to reject them if the evidence shows them to be obsolete or false. This process of elimination of useless information is just as essential to normal mental growth and activity as is the elimination of metabolic wastes to body development and well-being. Assimilation without elimination leads, in both cases, to perverted functions. Education must develop in the student the ca-

pacity for rapidly gauging the relative worth of facts and ideas. The process of sorting must go on continuously, and there must be no accumulation of obsolete relics of ideas to be occasionally examined and returned to storage in the treasure vaults of experience.

The facts must be tempered in the fires of experience to be of value in guiding future progress. The past and the present are two phases of the same continuity. The elastic force uniting the past and the present derives its quality and power from inspirational teaching. It is this which conditions men for unselfish devotion to the ideals which sustain human effort and enrich life. The power of inspirational teaching in shaping man's judgment, and in intensifying his purpose, is manifested in disciplined thinking and efficient leadership. It is this power which enables men to rise above defeat and discouragement, pressing on to the goal of high accomplishment in the struggle for human betterment. Knowledge of the facts of chemistry is essential in the process of making good chemists, but the inspirational element in teaching is indispensable to the transmutation of chemists into leaders of men.

CHEMISTRY AND THE POEMS OF ERASMUS DARWIN

GEORGE W. ECKERT

University of Missouri, Columbia, Missouri

ERASMUS DARWIN (1731–1802), naturalist, poet, and one of the greatest English physicians of his day contributed much to the interest in chemistry at a time when it was undergoing drastic changes. He formed the Lunar Society, which influenced the progress of chemistry both directly and indirectly, and included such members as James Watt, Matthew Boulton, William Murdock, James Kier, and Joseph Priestley. His poems of book length, *The Temple of Nature* and *The Botanic Garden*, contained many lines of chemistry and were accompanied by abundant notes explaining chemical principles. Several selections show his style of describing chemical action and theory in poetic form.

"Nymphs! you disjoin, unite, condense, expand,
And give new wonders to the Chemist's hand;
On tepid clouds of rising steam aspire,
Or fix in sulphur all its solid fire;
With boundless spring elastic airs unfold,
Or fill the fine vacuities of gold;
Or mark with shining letters KUNKEL'S name
In the pale Phosphor's self-consuming flame."

"Or mark how Oxygen, with Azote-Gas,
Plays round the globe in one aerial mass;
Or fused with Hydrogen, in ceaseless flow,
Forms the wide waves which foam and roll below."

"You taught mysterious Bacon to explore
Metallic veins, and part the dross from ore;
With sylvan coal in whirling mills combine
The crystal'd nitre, and the sulphurous mine;
Through wiry nets the black diffusion strain,
And close an airy ocean in a grain."

Darwin's works, which were written both to amuse and instruct, were very widely read and were also printed in foreign editions. In this way, the popularization of chemistry, as well as other sciences, was effected to some extent by Erasmus Darwin during the period about the beginning of the nineteenth century.

ERASMUS DARWIN

A RÉSUMÉ *of* ELECTRON DIFFRACTION

G. L. CLARK AND E. WOLTHUIS

University of Illinois, Urbana, Illinois

INTRODUCTION

WITHIN the past decade no discovery has proved to be more revolutionary in the field of physics than the fact of the wave character of all matter. The scattering of these material waves has developed into the new research tool called electron diffraction. This method of analysis of ultimate structures has already proved its worth, and now appears to be a necessary complement to the older method of X-ray diffraction. Together, these two methods of research are capable of solving many problems. It is the purpose of this paper to review briefly and yet completely the development of electron diffraction emphasizing particularly its applications to chemical analysis.

THE DE BROGLIE THEORY AND ITS VERIFICATION

In 1921, while studying the intensity of scattered electrons as a function of the angle of scattering, Davisson and Kunsman (*1*) observed certain unexplained maxima of intensity. This study of anomalous scattering intensities continued for some time without an adequate explanation (*2*). These results were not recognized as diffraction phenomena simply because no existing conception of electrons could comprehend such behavior. This bit of scientific history is a striking illustration of the need for a close relationship between theory and experiment. In 1924, quite independent of these scattering studies, de Broglie (*3*) proposed a wave theory of matter which was soon thereafter found to explain the problems of electron scattering as well as many others. We shall briefly review his contribution.

Ever since the entrance of the quantum hypothesis of light, there obtained a sharp dualism between the undulatory and corpuscular theories of light. Diffraction effects, particularly, spoke eloquently for the former; the photoelectric and Compton effects unmistakably indicated the latter. Many attempts were made to solve this difficulty. Rather than solving this dualism, however, de Broglie extended it to the material world, and sought to prove that it, too, possessed a wave nature as well as a corpuscular one. According to relativity, $E = m_0c^2$, and from the quantum theory we have, $E = h\nu_0$. De Broglie combined these into the form, $h\nu_0 = m_0c^2$. According to this purely mathematical relationship, ν_0 is characteristic of the wave associated with the particle (of mass, m_0) at rest. In this way a frequency was ascribed to a particle at rest. This frequency can be substituted in the equation for a stationary wave, $\psi_0 = \cos 2\pi\cdot\nu_0 t$. Now if we consider a moving particle, we must apply the Lorentz transformation and arrive at the equation:

$$\psi = \cos 2\pi \frac{m_0c^2}{h\sqrt{1-\beta^2}}\left(t - \frac{v}{c^2}x\right) \qquad (1)$$

which describes the plane waves associated with the particle moving with a velocity, v, and having a mass, $m = m_0 / \sqrt{1-\beta^2}$. On examining the properties of this wave system, we deduce the very important relationship:

$$\lambda = \frac{h}{mv} \qquad (2)$$

where λ is the wave length of the wave associated with a mass, m, traveling with a velocity, v.

Elsasser (*4*) at once suggested that such an equation could readily be verified by applying the test for any wave, namely its diffraction by a suitable grating. Experimental evidence accumulated rapidly in favor of the de Broglie theory. Davisson and Germer (*5*, *6*), in 1927, first showed that the heretofore anomalous scattering intensities of electrons *reflected* from a nickel crystal agreed fairly well with the expected maxima when the electrons of wave length, h/mv, are considered to be diffracted as are X-rays. The electrons used were accelerated by 30 to 600 volts, and the intensity maxima were registered electrically. Very shortly after the publication of this work, Thomson and Reid (*7*, *8*, *9*) reported additional experimental verification of the de Broglie equation, as obtained by the diffraction observed when electrons were *transmitted* through thin films. They used thin films of celluloid and several metals, electrons of 10–40 KV., and registered the diffraction maxima photographically. The agreement with the de Broglie equation was very good. Shortly after, Rupp (*10*) succeeded in diffracting electrons of 150–300 volts by transmission through thin metal films. The same investigator (*11*) was the first to diffract electrons of about the same energy by means of a ruled grating. In both cases the wave-length used was found to agree very well with the de Broglie theory. Worsnop repeated the verification by use of a ruled

grating (*12*) as well as by the use of thin foils (*13*). Further proof of the validity of the wave theory came with the experiments of Kikuchi (*14*) on mica, and of Ponte (*15, 16, 17*) who used powdered metallic oxide specimens, such as ZnO and MgO, and was successful in verifying de Broglie's law to within three parts per thousand. These early experiments were sufficient to establish the truth of de Broglie's conclusions. The diffraction of electrons was considered a fact, and immediately was applied to the study of many different types of substances, such as thin films of high molecular weight compounds (*18*), cellulose and its derivatives (*19*). Mark and Wierl (*20, 21, 22*) first succeeded in diffracting electrons by transmission through vapors.

APPARATUS

Full details regarding many kinds of construction can be found in the literature. There are, however, certain fundamental requirements which any apparatus for this work must meet:

(*a*) A monochromatic beam of electrons.

(*b*) A good vacuum.

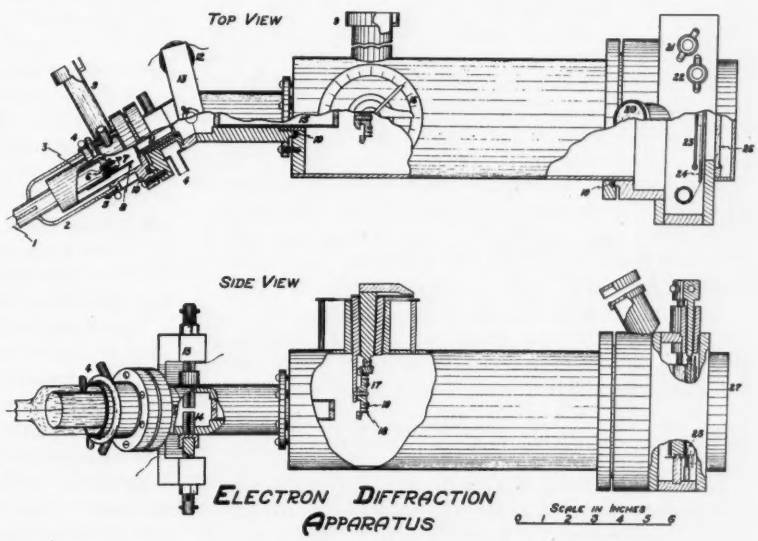
(*c*) Manipulation of the specimen within the evacuated apparatus.

(*d*) Electrical or photographic registration of diffraction maxima.

(*e*) A reliable measurement of the electron wave-length by sphere gap, standard substance or otherwise.

It is easily understood that, if the electron energy varies, the wave-length, too, will vary, and consequently no sharp diffraction maxima are obtained. One must, therefore, take the precaution of using a beam whose electrons are accelerated by a constant potential. Two principal methods have been used to obtain such an electron beam. In most cases the high tension current is rectified by means of a valve and smoothed by a suitable condenser. The cathode chamber is given the high negative potential and the body of the apparatus is grounded so as to make possible the manipulation of it during operation. This type of high tension supply has been used successfully by Thomson (*8, 23*), Ponte (*17*), Bragg and Darbyshire (*24*), Germer (*25*), Darbyshire and Cooper (*26*), and many others. On the other hand, one can make use of some sort of filter whereby only electrons of a definite energy are utilized out of a beam containing electrons of varying energy. Reid (*27*) chose to use an *electrostatic* field to serve as filter, and selected one component by placing a collimator in a suitable position to catch the electrons deflected through a certain small angle. Kikuchi (*14*), however, selected a homogeneous electron beam by using a *magnetic* field and collimator. More recently, Yamaguti (*28*) has made use of an electrostatic field selector quite similar to that used in some mass spectrographs.

The degree of vacuum necessary is quite dependent upon the operating voltage desired. Slow electrons, which are accelerated by a fairly low voltage, are easily deflected in their paths by molecules in the space they traverse. Consequently, the use of slow electrons requires the best possible vacuum conditions, generally obtained only by "baking" the whole apparatus for some time before assembly to insure the liberation of occluded gases from the surfaces. Generally, electrons of 10 KV. or more are used for most types of electron diffraction research, and the requisite vacuum can be obtained by an oil pump coupled with a diffusion pump of suitable capacity.



KEY TO FIGURE

1. Filament leads
2. Glass cathode arm
3. Brass shield
4. Cooling tubes
5. Picein joints
6. Mica insulation
7. Tungsten filament
8. Iron focusing shield
9. Evacuation ports
10. Rubber gaskets
11. Primary collimator
12. Solenoid
13. Soft iron core
14. Magnet poles
15. Secondary collimator
16. Graduated scale
17. Specimen wheel
18. Specimen pinhole
19. Specimen clamp
20. Observation window
21. Film winder
22. Shutter control
23. Shutters—door-type
24. Shield defining area of photograph
25. Photographic film
26. Fluorescent observation window
27. Brass cap

It is, of course, necessary to manipulate the specimen within the evacuated apparatus. The devices for this purpose vary greatly, being largely dependent on the type of specimen to be studied. A desirable feature is the design which permits both transmission and reflection studies to be made without "breaking" vacuum. This can be achieved by using a series of tapered brass or glass joints (*29*) or by employing a system of bellows such as described by Germer (*25*), Morgan and Smith (*30*), Finch and Quarrell (*31, 32*), and others. Several different specimens can be mounted on a specimen wheel, thus making possible the analysis of several substances during one operation or one evacuation.

The registration of diffraction maxima was at first accomplished by electrical means. Davisson and Germer (*5*) utilized a collector of the Faraday cylinder type, connected to a sensitive galvanometer. Today, except for certain experiments employing slow electrons, the photographic method is used in the large majority of cases. This procedure has the advantage of affording a permanent record of the diffraction effects. It can also be modified to make possible the registration of patterns of a standard and an unknown substance on the same film or plate beside each other, thus facilitating a comparison of the two patterns. This method has been a feature of the Finch and Quarrell apparatus (*33*). Such a comparison with a standard has the further advantage that it obviates to a large extent an uncertainty in the voltage of the electron beam, since one can calculate the voltage and wave-length of the electrons directly from the dimensions of a well-defined ring in the standard pattern.

Other methods to ascertain the voltage of the electrons employ either a spark gap of some sort or an electrostatic voltmeter. If the voltage, P, is known one can determine the wave-length, λ, of the electron by using the equation $\lambda = \sqrt{\frac{150}{P}}$ Ångstrom units.

Naturally, there is a wide diversity of modifications and improvements of apparatus suggested in the literature, too numerous to mention here. Only a few instances can be cited. Lebedeff (*34*) has suggested the application of magnetic focusing of an electron beam. Such a focusing was used to great advantage by Hughes (*35*) who verified de Broglie's law with electrons of 250 to 1000 KV., the source of the high-speed electrons being random. Finch and Quarrell (*31*) employed a focusing coil to facilitate the exploration of various parts of a specimen. Various types of cathodes for the production of the electron beam have also been proposed. They are of either the gas-ion, or the hot-filament kind, just as in X-ray tubes. The special requirements of an apparatus for the study of diffraction by vapors have also been met in a variety of ways. We refer the reader to the literature (*36–41*). A very convenient type of electron diffraction apparatus for the study of solid structures, designed, built, and used by the present authors, is diagrammatically represented in the figure (*149*).

SCATTERING OF ELECTRONS BY FREE ATOMS

To understand the diffraction of electrons by single atoms, molecules, or crystal lattices, it is necessary to consider the Schrödinger wave equation. The de Broglie theory was much amplified and generalized by Schrödinger, in 1926, in his wave mechanics, and by Heisenberg whose system of quantum mechanics was harmonized with the wave mechanics of Schrödinger. The Schrödinger wave equation has the general form,

$$\nabla^2 \Phi + \frac{8\Pi^2 m}{h^2} \cdot (E - V) = 0 \qquad (3)$$

which becomes

$$\frac{\partial^2 \Phi}{\partial x^2} + \frac{8\Pi^2 m}{h^2} \cdot (E - V) = 0 \qquad (4)$$

for the more specific case of wave motion in the X-direction, the moving particle possessing total energy, E, and potential energy, V (with respect to the field through which it is passing).

Now in applying this equation to the diffraction of electrons by atoms, molecules, or crystals, one substitutes definite space coördinate functions in the place of V in the Schrödinger equation, these functions describing the field in the diffracting object. This having been done, one proceeds to find appropriate solutions of the equation, and deduces therefrom the desired information concerning the angular distribution of the scattered electrons. We shall now consider individually the cases of scattering by the three types of scattering substances mentioned above.

Considerable light has been thrown upon the distribution of charge within an atom by the diffraction of electrons by free atoms. That such diffraction studies are capable of revealing something about the atomic structure is due to the fact that the atomic size and wave-length of the electrons are of the same order of magnitude, and hence interference between wavelets scattered from various parts of the atom is to be expected at certain angles. One cannot, therefore, assume the atom to be merely a point of scattering, and the amplitude of the diffracted ray to be independent of scattering angle. Born (*42*) and Mott (*43*) have developed expressions for the variation of the amplitude of the scattered wave with angle of scattering. We shall not attempt to develop the theory involved but only indicate the general methods used together with some results. By considering the contributions of an element of volume to the scattered wave and integrating over the whole volume of the atom we get a solution of the Schrödinger equation of the form:

$$\Psi = \Psi_0(r) + \frac{2\Pi m}{h^2} \int_0^{\infty}\int\int \frac{e^{ikr}}{r} \cdot V(xyz) \cdot \Psi(xyz)\, dxdydz \qquad (5)$$

This equation expresses, in general form, the intensity distribution of the scattered electrons. As in X-rays,

the integral of equation (5) is determined by the structure factor which governs the structure of the atom, or charge distribution. The electron diffraction structure factor takes the form:

$$E(\Theta) = \frac{me^2}{2h^2}\left[Z - F^+(\Theta) \cdot \frac{\lambda^2}{\sin^2 \Theta} \right] \qquad (6)$$

where $F^+(\Theta)$ is the atomic scattering factor for X-rays.

The experimental method of analysis involves the assumption of a certain structure or charge distribution, to calculate the factor E, the evaluation of Ψ, or the amplitude of scattering through various angles, and a comparison of this calculated amplitude with observed intensities, remembering that the intensity is proportional to the square of the amplitude. It must be remembered that the expression for the atomic scattering factor is strictly valid only for a *free* atom, and then only on the assumption that the incident wave is not deformed within the atom. This condition actually obtains only when using fast electrons. If slow electrons are used a correction must be made for refractive index.

In 1928, Dymond and Watson (*44*) began a study of electron scattering by monatomic gases as a function of the angle of scattering. This type of experiment was modified so as to make possible intensity measurements over large angles by Bullard and Massey (*45*) and Arnot (*36*, *46*). The former used argon for a scatterer, while the latter made extensive studies with mercury vapor and many other monatomic gases such as krypton, neon, etc. Using electrons up to 800 volts, Arnot plotted curves showing scattering intensity as a function of the scattering angle. The falling-off of intensity with angle was found to be very rapid. In general, the curves of the various monatomic gases are quite similar and the agreement with Born's theory is good, especially when the faster electrons are used. Certain peculiar humps in the curves obtained with the use of very slow electrons were not explained until a refractive index correction was applied (*47*).

If the electrons are fast enough, the scattering expressions cited above have been shown to be approximately correct for scattering by atoms in a crystal. Thomson (*48*) used a polycrystalline gold film, while Mark and Wierl (*49*) employed silver and aluminum films. Both investigators found the observed intensities to agree well with the calculated atomic scattering factors.

The studies pertaining to the scattering of electrons by single atoms are not numerous. They do show a close analogy between electron and X-ray scattering. It is well to remember, however, that the efficiency of electron scattering is about 10^{-7} times that of X-rays.

SCATTERING OF ELECTRONS BY FREE MOLECULES

Debye (*50*) developed the theory governing the scattering of X-rays by gases. Experiment showed that long exposures were necessary for the registration of the diffraction maxima which are characteristic of the inter-atomic distances within the molecule.

The distribution of scattering intensity can be computed, as before, by substitution of appropriate values of V in the wave equation. It is important to remember that most molecules, unlike atoms, are not spherically symmetrical, so that integration over the whole volume of the molecule is somewhat more difficult. Also, one must reckon with the fact that these unsymmetrical molecules are oriented randomly with respect to the incident electron beam. A typical calculation has been made by Massey (*51*) for the scattering of relatively fast electrons by hydrogen molecules. It is found that the calculations are entirely analogous to those used with X-rays, as developed by Debye, and amplified by Mott (*43*) and Bethe (*52*). The intensity of scattering at an angle is given by

$$I_\Theta = k \sum_i \sum_j E_i \cdot E_j \cdot \frac{\sin x}{x} \qquad (7)$$

where k is a constant, E_i and E_j are the amplitudes of the waves scattered in the direction Θ by the i and j atoms, respectively, and

$$x = \frac{4\pi d}{\lambda} \cdot \cos^2 \Theta/2$$

where d is the distance between atom i and atom j in the scattering molecule.

The method used in the experimental determination of molecular structure by electron diffraction has been adequately stated in the literature (*40*, *41*, *53*, *54*). The apparatus is simply a modification of that used in working with solids. A jet of vapor passes through the electron beam and is condensed on a surface cooled with liquid air in order not to disturb the vacuum in the apparatus. Good patterns are obtainable in a few seconds, or even in a fraction of a second in some cases. Fast electrons are usually employed because their use obviates any consideration of inelastic collisions. The importance of incoherent scattering has been worked out theoretically by Morse (*55*) and Bewilogua (*56*). However, this effect can be ignored when electrons of sufficient energy are used. The method of interpreting the photographs differs quite considerably from that employed in the cases of solid or crystalline diffracting substances. Essentially it involves the *assumption* of a certain molecular structure and inter-atomic distances within the molecule, the *calculation* of the interference intensities expected from such a structure, and a *comparison* of the calculated with the observed intensities to establish the identity of the assumed model with the actual molecule. Pauling and Brockway (*54*) have studied the merits of the various methods for evaluating the intensities in a photograph, and point out that visual methods are accurate to within about one per cent.

Many and various are the molecules which have been subjected to this type of analysis. De Laszlo (*57*) has pointed out that any substance having a vapor pressure of at least 10 cm. of mercury at 750° can be examined by

electron diffraction. Mark and Wierl (*20, 53, 58*) were the first to diffract electrons by gases and vapors. They first studied CCl_4 and obtained several maxima which indicated a tetrahedral structure for the molecule. Twenty other halides were reported in the same paper. Inter-atomic distances were readily found, and from these were deduced the sizes of the atoms in the molecule. Cosslett (*59*) made a thorough study of CCl_4 and succeeded in getting seven orders of diffraction. Likewise, Arnot (*60*) has studied this compound together with bromoform and the halogens. Many other halogen compounds have been investigated. Sutton and Brockway (*61*) examined the structure of chlorine monoxide, oxygen fluoride, methyl chloride, dichloromethane, and chloroform with the purpose of testing the constancy of the C—Cl bond angle, and also to prove the additivity rule of atomic radii proposed by Sidgewick and Pauling. Some alkyl halides studied were reported by Bru (*62*). One of the early problems to receive attention is that concerning the probability of two stereoisomeric forms of dichloroethane. Wierl (*63*) at first believed he had distinguished two Cl-Cl distances in the molecule which he interpreted as due to two different forms. On the basis of theoretical considerations, Bergmann and Engel (*64*) disproved the existence of two stable stereoisomeric forms of this molecule, a conclusion in which Wierl (*58*) has also concurred. Dornte (*39*) has reported on his investigations of the halogen derivatives of ethylene, and Wierl (*58*) has identified the *cis* and *trans* forms of dichloroethylene. Inorganic halides such as those of sulfur and mercury have been studied by Braune and Konke (*37*) and Brockway (*65, 66*).

Oxygen-containing organic compounds have been used frequently to diffract electrons, for the purpose of studying the nature of the C—O bond and bond angle. Bru (*67*) investigated the structures of formaldehyde, and the methyl and ethyl ethers. The C-O distance in the aldehyde is 1.15 Ångstroms, while in the ethers it is about 1.34 Ångstrom units, the latter varying somewhat with the alkyl group. The C-O-C angle was found to be about 100° in the case of the ethers. Sutton and Brockway (*61*) reported that this angle increases with the weight of the alkyl groups involved. According to Dornte (*38*), the study of such compounds as carbonyl sulfide, chloride and bromide, and also acetyl chloride and bromide, indicates that the C=O bond in these carbonyl compounds is quite constant. Thermochemical data have indicated two possible structures for formic acid, implying a resonance of the double bond between the carbon atom and the two oxygen atoms. Recent work by Pauling and Brockway (*68*) has confirmed the existence of such a resonance. They, as well as Hengstenberg and Bru (*69*), have identified the polymers of formic acid. The structures of methyl azide and carbon suboxide (*70*), as well as those of cyanogen and diacetylene (*71*) have been deduced from electron diffraction patterns. The diacetylene patterns give evidence of a doubling of the molecule as was first suggested by Wierl (*58*). Paraldehyde appears to possess a staggered six-membered ring of alternate carbon and oxygen atoms, according to Carpenter and Brockway (*72*).

In an interesting study of iodine and the di-iodo benzenes, Hendricks and his associates (*40*) have shown that the I-I distances for the substances in the vapor state are the same as those in the solid state, the latter being deduced from X-ray data. There is also evidence of a "steric-hindrance" effect in the case of the orthodiiodobenzene where the I-C-I angle is about ten degrees from the expected symmetrical position. This investigation points the way to other studies on the steric effect.

The oxides of nitrogen, N_2O, NO_2, N_2O_4, and N_2O_5, were studied by Maxwell and his associates (*73*), and a structure was assigned to each. Wierl (*74*) determined the structures of CO_2, CS_2, and SO_2.

Very recently Brockway and Jenkins (*75*) have published the results of their study of the methyl derivatives of Si, Ge, Sn, Pb, N, S, and Hg. Still more recently, Pauling and Brockway (*76*) have reported on the investigation of the compounds, methyl azide, methyl nitrate, and fluorine nitrate, with the particular purpose of testing the adjacent charge rule suggested by Pauling.

A number of other gases and vapors have also been subjected to electron diffraction analysis, but we shall mention no more specific cases here. The examples cited above are ample to show the versatility of the method and its efficiency in probing the inner structure of every kind of molecule which can be vaporized appreciably.

SCATTERING OF ELECTRONS BY CRYSTALLINE AND SEMI-CRYSTALLINE SUBSTANCES

In the remainder of this review we shall survey the work done on crystalline and semicrystalline substances, and also mention some of the more practical applications of electron diffraction analysis.

As in the previous cases of electron scattering by free atoms or molecules, so too in the theoretical treatment of the interaction of an electron with a crystal, one inserts the proper V value in the Schrödinger wave equation, solves for the scattered wave and deduces from it the angular distribution of scattering intensity. In the first cases of electron diffraction by crystalline substances, the simple method of substituting the de Broglie wave-length in the Bragg equation was used. Many subsequent investigators followed this precedent, and generally the agreement with experiment was good so long as fast electrons were employed. This method has been found a reliable one in the hands of such men as Kikuchi, Kirchner, Ponte, Rupp, Thomson, and others who usually employed electrons of at least 15 KV.

The first attempt at a more accurate approach to the problem was made by Bethe (*52*) who considered the crystal lattice to possess a potential which will determine the V value in the wave equation. If the energy of the incident electron beam is not very great, the

average inner potential of the crystal will exert a refractive effect upon the electrons. The refractive index can be expressed by the relationship,

$$\mu = \sqrt{1 + \frac{\Phi_0}{P}} \tag{8}$$

where Φ_0 is the mean inner potential, and P is the voltage of the electrons. It corresponds to the index of refraction for X-rays as developed by Siegbahn and Stenström for precision measurements, but is much more significant for reliable calculations in electron diffraction. For example, for electrons of wave-length, 0.39 Ångstrom units (*i. e.*, 1000 volt electrons), μ becomes 1.01, whereas for X-rays of the same wave-length the difference from unity is only 5×10^{-6}. Again, for electrons of wave-length 3.88 Ångstrom units (*i. e.*, 10 volts), μ becomes 1.58. From these figures one can readily see that the wave-length of slow electrons is decreased very appreciably within the diffracting crystal lattice, with the result that the diffraction maxima should be displaced toward the central, undiffracted beam. Such a displacement was, in fact, observed by Davisson and Germer in their pioneer experiments, and was explained on the basis of the refractive effect by Bethe (*52*) and also by Eckart (*77*).

Almost all the experiments designed to throw light upon the refractive effect of the crystal potential upon the electron beam have been performed with single crystals. The following is the experimental method. Suppose a beam of electrons strikes a crystal at an angle Θ, and the refracted ray makes the angle Θ' with the crystal face. It can easily be shown that,

$$P \sin^2 \Theta = \frac{150\, n^2}{4d^2} \cdot \Phi_0 \tag{9}$$

where P is the voltage of the electron beam, n is the order of diffraction, d is the interplanar spacing, and Φ_0 is the inner potential of the crystal. Experimentally, one observes the positions of the various orders of reflection (obtained by rotating the crystal face around an axis normal to the beam), and plots $P \sin \Theta^2$ against n. Then the intercept on the $P \sin \Theta^2$ axis gives the value of Φ_0 directly. Or one can vary P, the voltage, and keep Θ constant and again find Φ_0 in the same way. This latter method is usually employed with slow electrons. Working at low voltages, measurements of inner potential have been made by Davisson and Germer (*78*), Rupp (*79*), Farnsworth (*80*), Dames (*81*), Ehrenberg (*82*), and others. Most of them used single metal crystals. Measurements at higher voltages have been reported by such workers as Shinohara (*83*), Yamaguti (*84*), and others. We can only generalize the results here. Tillman (*85*), in a study of the effect of electron voltage (or wave-length) upon the inner potential values, has shown that the inner potential measurements agree very well. In general, the inner potential is a constant characteristic of a crystal, independent of the voltage of the electron beam, although Farnsworth (*80*) has cited some evidence to the contrary. It has been shown (*86*) that anomalous values of Φ_0 are sometimes due to space charges of electrons, particularly when non-metallic substances are employed to reflect the electrons. Also, generally the consistency in the Φ_0 values is better when fast electrons are employed in the experiments. The inner potentials of most crystals lie somewhere between 10 and 20. This includes values not only for metals but for many other types of crystals such as rock salt, pyrites, calcite, fluorspar, zinc blende, etc. Recently, accurate measurements of inner potential by Yamaguti have indicated that Φ_0 varies slightly at small angles of incidence when pyrites were used, probably indicating a variation of inner potential with depth in the crystal, or perhaps a layer-type of potential distribution.

The foregoing refers to inner potential studies in which single crystals were used to reflect slow electrons. Many other interesting effects have been observed in single crystal investigations. For instance, Farnsworth (*80, 87*) has carried on extensive studies of copper, silver, and gold crystals. He observed several maxima in addition to those expected theoretically. Certain interferences were explained by the simple theory of diffraction, using a zero inner potential for the crystal, that is, a refractive index of unity. Some of these indicated half-order reflections, or what is equivalent to a doubled spacing of the surface layers. Similar "forbidden" orders were observed by Rupp (*79*). They have been attributed to surface films of gases because of the observation that heating the specimen caused their disappearance. Recently, Finch and Quarrell (*88*) have proposed that the "extra" rings are due neither to gas films nor reflection from forbidden planes, but to the external crystal shape, that is, to boundary faces through which the electron beam leaves the crystal.

Using single crystal faces of Fe, Ni, and W, Germer (*89*) observed some reflection of fast electrons even when the glancing angle differed somewhat from the Bragg value. He suggested that the accuracy with which this angle must be adjusted is a measure of the degree of imperfection in the crystal face, this imperfection being especially prominent at the surface.

Single crystal patterns are usually characterized by certain black and white lines called Kikuchi lines. Kikuchi (*14*) first observed this effect when fast electrons were transmitted through mica. Three different patterns were obtained, the differences depending only on the thickness of the films of mica. The thinnest films (10^{-6} cm.) produced the "N-pattern" with a net-like arrangement of spots in three parallel lines at sixty degrees to each other. Films thick enough to show interference colors gave rise to the "L-pattern" which consisted of a number of spots lying on circles, and also several black and white lines. These lines persisted when the thickness of the film was still further increased to give rise to the "P-pattern." The generally accepted explanation of the lines has been given by Kikuchi. He assumed that they resulted from diffuse

scattering of the electrons and reflection of the diffusely scattered rays by the planes within the film. This explanation does not completely cover the subject, however. These same Kikuchi lines obtained by reflection of electrons from crystal cleavage planes have been used in calculating the inner potential of a crystal (*83*). The "N-pattern" is accounted for if the diffraction is considered to be caused by a cross-grating; that is, the third Bragg diffraction condition becomes relaxed for such thin films. How this can be explained has been shown by Bragg (*90*) who postulates a distortion of the crystal. As the crystal becomes thicker the distortion decreases. Darbyshire (*91*) has also conducted a thorough study of the patterns obtained from mica.

As we have mentioned before, these Kikuchi lines are found in reflection patterns from nearly all single crystals. Nishikawa and Kikuchi (*92*) have reported such results for calcite, topaz, and other crystals. Emslie (*93*) was unable to obtain the Kikuchi lines by reflection from galena, a conductor, but also observed them for calcite. However, Germer (*94*) has very recently succeeded in obtaining the Kikuchi pattern with galena. He also found that etching of the cleavage face previously polished showed some orientation of surface crystallites, very likely due to the polishing. Incidentally, Hopkins (*95*), in a similar study of a calcite cleavage face, has shown that polishing considerably distorts the surface structure and causes a broadening of the Kikuchi lines, whereas subsequent etching again causes the appearance of very sharp Kikuchi lines.

Single crystals have also been used in producing one- and two-dimensional electron diffraction patterns. Attention has already been directed to the cross-grating, or two-dimensional effect observed by Kikuchi with mica and explained by Bragg (*90*). One must not press too far the analogy between X-ray reflection and electron reflection from a crystal face, because the third diffraction condition is usually much relaxed for electrons whose penetrating power is small. Kirchner and Raether (*96*) have discussed the various effects produced by relaxation of the diffraction conditions. Thomson (*97*) obtained cross grating patterns by reflecting fast electrons at glancing incidence from etched crystals of silver and copper. All the spots on the patterns seemed to be due to reflections from planes in a single zone, suggesting that the beam very likely passed through these projections on the surface. Germer (*89*), however, prefers to consider the pattern to be due to reflection from small crystal blocks set at a variety of angles to the surface, although such an explanation makes the observed Kikuchi lines impossible. Later experiments on galena by the same author (*94*) confirmed him in his opinion that the pattern of spots is due to imperfection of crystal surface rather than thinness. He employed "rocking curves" to distinguish between the two possibilities.

One-dimensional electron diffraction has presumably been observed by Emslie (*98*) at certain positions of a stibnite crystal. Tillman (*99*) also obtained certain patterns from zinc blende which he interpreted in a similar way as arising from a one-dimensional effect. However, Finch and others (*100*) have attempted to explain the observed interferences in terms of envelopes associated with Kikuchi lines. Still other suggestions have been made, but a satisfactory explanation is still wanting.

Reflection of electrons from polycrystalline surfaces produces rings typical of a "powder" pattern. The sharpness of the observed rings seems to indicate that such a pattern is really due to transmission through randomly oriented projections on the crystalline surface. This is, in effect, what happens when a beam of electrons is diffracted by transmission through a thin film. Actual reflection from the crystallites in a polycrystalline surface would very likely produce a series of blurred rings due to lack of penetration into the surface.

We shall now discuss some of the important practical applications of electron diffraction. We have been considering the more theoretical studies using, for the most part, single crystals, both slow and fast electrons, and reflection methods generally. Through such experiments much light has been shed upon the mechanism of electron diffraction and the way it differs from, and compares with, X-ray diffraction. It is our purpose now to consider some of the great variety of ways in which electron diffraction has clarified many problems concerning polycrystalline structures and their changes with treatment. In most cases the ordinary methods used in X-ray analysis have also been applied in this type of work with electrons; that is, the de Broglie wave-length has been substituted in the Bragg equation for diffraction, such effects as inelastic scattering, refractive index, and so forth being ignored. This introduces but very little error because of the high speed of the electrons usually employed.

Metallic specimens to be used for transmission of electrons must be very thin and can be prepared by various methods. Some of them are: etching of metal leaf or foil by floating it on a suitable solvent, sublimation of the metal by heating in vacuum, chemical deposition (*e. g.*, Ag from an ammoniacal solution), anodic thinning in an electrolytic cell, and various others. Ordinary commercial gold leaf needs but very little thinning with KCN to make it suitable for diffraction by transmission. Deubner (*101*) has prepared thin films of Ag, Au, and Cu by winding thin wires of these metals around a tungsten wire filament and evaporating them on to a support by passing a current through the filament *in vacuo*. Other modifications of the methods of preparation cannot be discussed separately here.

The type of pattern a metal gives is largely a function of crystal size and the degree of orientation in the film. The latter, in turn, is again dependent upon the temperature, the degree of working and the substrate on which it is formed. Thomson (*8*) first used Al and Au films as diffraction gratings to confirm the de Broglie theory. Ironside (*102*) continued this work, using Ag, Cu, and Sn films. Trillat and Hirsch (*29*) have made

a detailed study of Au and Pt films. They found that at times a good powder pattern was obtained, at other times the patterns indicated considerable orientation, and occasionally a sufficiently large single crystal gave rise to a single crystal pattern. The beaten films revealed an orientation of either the (100) or (110) directions of these cubic crystals normal to the surface of the films.

Particular emphasis has been placed upon the factors influencing the orientation of the metal crystallites. The temperature effect upon Au and Pt films has been investigated by Trillat and Hirsch (*29*) who found that the medium in which the metal was heated had a profound effect upon the change taking place. Heating *in vacuo* increased the orientation and caused the formation of a single crystal. However, the presence of air during heating produced a pattern they interpreted as due to an oxide in the case of gold. A similar study of the temperature effect upon Au and Ag films was conducted by Preston and Bircumshaw (*103*), who tried atmospheres of air and hydrogen, and also vacuum. They concluded that recrystallization and reorientation takes place when the films are heated in air, presumably due to the oxygen in the air. In hydrogen and vacuum no such changes were observed. Dixit (*104*) also studied the effect of the temperature upon the orientation in Al, Zn, and Ag films, and determined the type of crystallite arrangement in each. Using reflection methods, Thomson (*105*) early recognized the effect of the substrate upon the orientation of deposited metals and other substances. Silver, deposited on a rock salt crystal (*106*), is oriented with the cube face parallel to the face of the crystal. Very recently, Bruck (*107*) has reported on a comprehensive study of the effect a substrate has upon the metal deposited on it. Metals such as Ag, Au, Al, Cu, Ni, and others have been deposited by sublimation *in vacuo* upon rock salt and upon amorphous or polished surfaces. It was found that the temperature at the time of deposition affects the degree of orientation very markedly. Also, when one metal is deposited upon another, the similarities of the two atoms and the lattices involved have much to do with the orientation. However, the difference between the two lattice parameters has an effect only when it is quite large. Prins (*108*) has attempted to correlate the diffraction pattern with the type of metal crystal lattice giving rise to that pattern. An investigation on platinized asbestos by Richards (*109*) has shown that the Pt rings show up in the pattern only after a high degree of platinization has been attained. Apparently the asbestos fibers split open to increase the ratio of asbestos to Pt surface exposed to the electron beam. Of an entirely different nature is the study by Trillat and Motz (*110*), who showed that the anomalous diffraction rings in many metal patterns are due to surface contamination by organic substances.

Some of the first substances to be examined were metallic oxides. Such specimens are prepared in a variety of ways. A metal may be melted and the oxide film on its surface caught on a wire loop drawn up through it. If the metal has a tendency to ignite in air, it is covered with a zinc chloride flux. This procedure has been used by Bragg and Darbyshire (*24*) and also by Cooper (*111*). They have also used a method suggested by Ponte (*15*), namely, collecting the oxide vapors from the ignited metal on some sort of support. Or a foil may be clamped between two pieces of metallic gauze and heated; the foil cracks due to oxidation, and the gaps are bridged by transparent oxide films. Ordinary tin wrapping foil can be made to give suitable SnO_2 specimens in this manner. Occasionally the reagent oxides can be powdered and sprinkled on to a fine-mesh gauze. Still another method for preparing thin films of oxides is to heat a piece of metal until interference colors appear on the surface; this oxide film is then removed by electrolytic corrosion (*112*). This method works particularly well for the preparation of Cu_2O and NiO films (*113*, *114*).

Of the various oxides studied, ZnO has received more than ordinary attention especially with a view to determining its desirability as a standard in electron diffraction. Bragg and Darbyshire (*24*) examined the pattern given by ZnO prepared by the "loop" method and found it to give evidence of some abnormal form of the oxide, perhaps cubic. It has been determined (*32*) that the hexagonal ZnO formed by the "loop" method is usually separated from the underlying zinc metal by a pseudomorphic form of ZnO. Such a modification is not obtained by "smoking" ZnO on to a Cu or Ni gauze. Incidentally, the pseudo-form of ZnO changes to the normal type of lattice when it is heated. Yearian (*115*) has studied the intensities of the ZnO interferences with a view to establishing the shapes of the atoms within the crystal lattice.

Electrolytic corrosion has served well in separating Cu_2O and NiO films from the respective metals. These are cubic structures whose parameters are not influenced by the underlying metals (*116*). Murison (*117*) reported a peculiar oxide of copper formed by heating a film of Cu_2O in a furnace through which air circulated. A change occurred to produce a "three-ring" pattern, easily converted back to Cu_2O by grinding.

Many other oxides have given data in good agreement with X-ray results. Oxides of Pb, Cd, Mg, and Al have been prepared by the "loop" method, and their lattice constants were found to agree with the accepted values (*24*, *111*). Quite recently Verwey (*118*) has examined the oxides of aluminum and found that the patterns indicated various degrees of crystal perfection ranging from the amorphous (γ'-form) to the completely arranged cubic lattice. When Al_2O_3 hydrate is heated at 900° a structure results which is intermediate between the γ and the cubic form. The surface film on heated iron, after its removal by electrolytic corrosion, proved to be Fe_3O_4 plus some γ-FeOOH (*114*). Heating at 600° caused a change to a pattern like that of γ-Fe_2O_3 as indicated by a comparison of intensities. Cates (*119*) confirmed this latter result by showing that rust, or γ-FeOOH, changed to γ-Fe_2O_3 when heated.

A few other inorganic substances have been examined by electron diffraction, but these cases do not warrant a special mention here.

A large number of organic compounds, as well as carbon itself, have been subjected to this type of analysis. Mongan (*120*) examined graphite and amorphous carbon with a view to determining their particle sizes. Amorphous carbon specimens were prepared by wafting a copper gauze through a luminous flame. He found the widths of the diffraction rings to be definitely related to the size of the colloidal particles, contrary to Trendelenburg's observations (*121*). The specimens of amorphous carbon exhibited the same interferences as graphite although the rings were less intense and not so well defined. Using the equation of von Laue and of Scherrer, he was able to calculate the amorphous carbon particle size to be about thirty Ångstrom units. Recently, the effect of oxygen upon graphite at high temperatures has been investigated (*122*). Other studies on graphite will be mentioned in connection with the work on the polishing mechanism and lubrication.

We have already noticed the versatility of the electron diffraction method in dealing with organic substances in the vapor phase. For work in the solid state thin films may be prepared by dissolving in a suitable solvent and spreading this solution on water or mercury. Other methods have also been employed in preparing the thin films of organic materials.

Much of the work of this type has been done by Trillat and his associates (*123*, *124*). The studies of hydrocarbon structures have generally confirmed the X-ray results for these compounds. Electron diffraction has been found to bring out the orientations of long-chain compounds very clearly, even with monomolecular layers (*110*). The degree of orientation with respect to a metal base has been shown to be greater the longer the chains. In comparing the orientations of paraffins and stearic acid on water, Trillat and Hirsch (*125*) found, by inclining the films to the electron beam, that the hydrocarbons are oriented with their C-axis normal to the water surface, whereas stearic acid is oriented obliquely with respect to this surface. Very direct measurements from the pattern of the paraffins indicated a cross-sectional area of 4.84 × 7.30 Ångstrom units. The chemical nature of a surface has much to do with the orientation of paraffins or the fatty acids upon it. For example, aliphatic chains with no functional terminal group have a tendency to spread out on surfaces devoid of functional groups. But these same compounds do not spread out on water in this manner. Murison (*126*) has deduced a value of 2.54 Ångstroms as the carbon-to-carbon distance in the paraffin chain. This periodicity is characteristic of such things as vaseline, many greases, picein, and other substances like them. Rubbing of these materials tends to increase their orientation. Similar studies of the hydrocarbon structure and orientation have been made by Nelson (*127*).

The three forms—α, β, and γ—of the fatty acids have been recognized by electron diffraction (*123*) confirming the X-ray identification of these modifications. As has been mentioned, the monobasic fatty acids tend to orient obliquely with respect to the supporting surface. The di-acids usually lie flat upon the support. These effects are explained by the affinity of the functional —COOH group for the surface supporting it. Murison (*126*) has conducted a survey of several kinds of thin organic films, particularly of long-chain compounds, and has discussed the significance of the different types of patterns. Incidentally, it might be pointed out that the basal-plane dimensions of these long chain molecules are more directly computed from electron diffraction patterns than from X-ray photos especially when thin, well-oriented films are used for the transmission of electrons. This is due to the fact that a very small Bragg angle is necessary for the reflection of fast electrons and only the (hko) planes register when a beam is transmitted through a film in which the long-chains are oriented normally, or nearly so, to the surface of the base. Very recently, Storks and Germer (*128*) have investigated the inclinations of various long-chain compounds to the surface normal. The degree of inclination is believed to be related somewhat to the degree of saturation of the chains in lard. Stearic acid and its esters possess different inclinations.

Considerable work has been done on cellulose and its derivatives. Thomson and Reid were the first to examine a thin celluloid film, prepared from an amyl acetate solution, and observed three orders of the spacing 4.46 Ångstroms (approximately). Kirchner (*18*) succeeded in getting fairly good patterns of celluloid and nitrocellulose, including a single crystal pattern of the latter. Dauvillier (*19*) likewise obtained diffraction patterns from nitrocellulose, cellulose acetate, and related substances. Different orientations or fibering appeared, depending upon whether the film had been evaporated from its solution on mercury or on water. Jones (*129*) has carried out an extensive study of the structure of thin celluloid films, and has computed a structure from single-crystal patterns. In working with such compounds as highly nitrated cellulose, cellulose triacetate, cellulose tripropionate, and others, Trillat (*130*) found that fresh films which are amorphous become crystalline on standing. Very likely other organic polymers, such as rubber, proteins, gelatin, and others, crystallize in a similar way. The structure of the cellulosic materials was also worked out. The chains are parallel to each other and to the surface of the film. The values a and b were derived from the patterns produced with the beam normal to the film surface. They are, $a = 7.1$, $b = 4.68$ Ångstrom units. By inclining the film to the beam, c turned out to be 2.5 Ångstrom units.

Rubber, too, has been studied by Trillat and Motz (*131*). As in X-rays, two patterns were obtained, one from an unstretched, another from a stretched specimen. Difficulty is encountered in stretching the extremely thin films. The "crystalline" pattern appeared with less stretching of the rubber than is re-

quired to bring out the X-ray fiber pattern. The dimensions found are: c = 8.1, a = 12.4 Ångstrom units. These values agree well with those of Meyer and Mark who used X-ray methods.

There remains to consider briefly some of the more practical and unique contributions based on electron diffraction methods. Much interest has centered about the question of an amorphous layer on the surface of polished metals. Naturally, in this type of study, diffraction is by reflection only. Raether (*132*) has shown that rubbing a metal surface with fine emery tends to reduce the grain size of the surface metal as is indicated by broad rings in the pattern. Using such metals as Cu, Ag, Au, and Cr, French (*133*) determined that the polished surfaces of all of these metals gave rise to the same two broad diffraction rings neither of which was related to the metal's crystal lattice dimensions. This confirmed the existence of a liquid, or Beilby layer of metal, so-called after Beilby who first postulated it on the basis of microscopic evidence. Boas and Schmidt failed to detect such a layer when using X-rays to study the surfaces of polished metals, undoubtedly due to the fact that the X-rays penetrated to, and revealed, the metal underneath it. Darbyshire and Dixit (*134*) found the change to the "amorphous" pattern accentuated by polishing bismuth and other trigonal metals; in these cases a pronounced change of spacing occurs. These polished metals again showed the same two diffuse rings as observed when cubic metals were used, thus substantiating the evidence for a Beilby layer. Calculations seemed to indicate a monatomic liquid layer. Etching of the polished surfaces restored the crystalline pattern in all cases. Germer (*135*), however, voiced a dissenting opinion in this type of research. He reported that an "amorphous" pattern results when the electron beam is reflected from the metal in a direction parallel to the tiny ridges on its surface. If the surface has none of these ridges, no pattern can be obtained. In other words, all reflection patterns are due to transmission of electrons through the ridges of metal on the surface. On the other hand, subsequent experiments by Finch, Quarrell, and Roebuck (*136*) again presented a powerful argument in favor of the Beilby layer. They found that zinc flashed on to a *polished* copper surface lost its power of producing a crystal pattern almost at once, while zinc flashed on to an *etched* copper surface retained its crystalline structure. In the former case, the zinc apparently "dissolved" in the liquid copper surface. In looking over the evidence given, we conclude that the preponderance of opinion favors the Beilby layer theory. It is obvious that this is specifically an electron diffraction problem. A résumé of the progress in this field has been published by Bates (*137*).

Another interesting application of electron diffraction is in the evidence of lubrication. Jenkins (*138*) thoroughly investigated the mechanism of graphite lubrication, and found that rubbing a graphite surface caused considerable orientation of the crystallites as is shown by short arcs in place of diffraction rings in the pattern. On the other hand, the same treatment of amorphous carbon gave no orientation except after prolonged polishing, indicating that the amorphous carbon consists perhaps of aggregates of very small graphite crystals. Lubrication by means of oil containing colloidal graphite caused the deposition of a smooth film of graphite on the bearing surfaces.

Murison (*126*) has been interested particularly in the behavior of long-chain molecules in lubricating substances. He has analyzed the different types of patterns usually obtained from such things as greases, heavy oils, fatty acids and alcohols, and the lighter oils. In general, mixtures of hydrocarbons showed more tendency to orient than pure substances. Where orientation is prominent there seems to be a strong affinity between the lubricant and the metal surface, which makes for the retention of the lubricant. It also appears that lubricating power is enhanced by the use of substances with a high molecular weight. A recent study by Andrews (*139*) on the orientation of the molecules of lubricating oils has revealed some interesting facts. Some orientation of "cracked" oils is the result of oxidation, a little of which is desirable at times for better lubrication. But a slight relationship, if any, exists between viscosity and orientation in the oils. It was also found that all metals do not behave alike in affecting the orientation of oils upon them. Chromium and nickel were found to be more resistant to corrosion by oils than iron and steel. Other investigations of liquids by electron diffraction have been conducted by Maxwell (*140*). He pointed out that the liquid must have a low vapor pressure, and a suitable surface tension and viscosity. The film of oil was held in a wire loop for transmission of electrons. All the liquids gave rise to the same three broad interferences of spacings 4.63, 2.1, and 1.2 Ångstroms, agreeing fairly well with Stewart's X-ray results for $C_{15}H_{32}$ and similar compounds.

Catalysis, which up to the present is still quite a mystery, may some day be clarified as the result of electron diffraction research of surface changes during reactions. Already in 1929 Germer (*141*) showed that gases enter the crystalline lattices of metals on which they are adsorbed. Rupp (*142*) studied the preferential adsorption of gases by various metals and confirmed the results of Germer's work. Hydrogen was found to enter the nickel lattice and distort it whereas nitrogen does not do this. He examined the surface of a nickel catalyst during the synthesis of ammonia from hydrogen and nitrogen. The hydrogen first enters the nickel lattice and is then capable of combining with the nitrogen. Other similar problems await a solution by this method of study.

The passivity of certain metals has usually been attributed to an oxide film (*112*). Rupp and Schmid (*143*) attributed five interference maxima to the passive layer on iron, but were unable to obtain conclusive evidence of an oxide layer (*144*). Later, Rupp (*145*) expressed the opinion that the passivity of iron may be due to a close-packed structure of γ-Fe_2O_3 on its surface.

Particle size has also been determined in a manner analogous to that used with X-rays. Von Laue (*146*) has discussed critically the original work by Thomson (*97*) on this subject. A comparison of X-ray and electron diffraction methods for determining particle size has been made by Brill (*147*). He has developed the theory to show that a noticeable widening of lines produced by the diffraction of electrons is only effected by much smaller crystals than in the case of an X-ray determination. He also pointed out that *fast* electrons must be used in this work in order to avoid only surface registration.

A unique bit of analysis has been reported by Rollier, Hendricks, and Maxwell (*148*), who have succeeded in determining the crystal structure of the radioactive element, polonium, by means of electron diffraction analysis. Since not enough polonium was available for an X-ray examination of its structure, 10^{-7} grams of it were condensed upon a thin collodion membrane, 3 millimeters square, and its diffraction pattern recorded by transmitted electrons. The pattern resembled that of tellurium, and the structure seems to be a pseudo-hexagonal lattice with the dimensions, $a = 4.25$, $c = 7.06$ or 14.12 Ångstrom units. The true lattice, they report, is perhaps a monoclinic structure. If this is so, it will be unique among the structures of the elements, all of which are cubic, tetragonal, or hexagonal.

LITERATURE CITED

(1) DAVISSON, C. AND C. H. KUNSMAN, *Science*, **54**, 522 (1921).
(2) DAVISSON, C. AND C. H. KUNSMAN, *Phys. Rev.*, **19**, 253 (1922); *ibid.*, **22**, 242 (1923).
(3) DE BROGLIE, L., *Phil. Mag.*, **47**, 446 (1924); *Ann. phys.*, (10), **3**, 22 (1925).
(4) ELSASSER, W., *Naturwissenschaften*, **13**, 711 (1925).
(5) DAVISSON, C. AND L. H. GERMER, *Phys. Rev.*, **30**, 705 (1927); *Proc. Nat. Acad. Sci.*, **14**, 317 (1928).
(6) GERMER, L. H., J. CHEM. EDUC., **5**, 1041, 1255 (1928).
(7) THOMSON, G. P. AND A. REID, *Nature*, **119**, 890 (1927).
(8) THOMSON, G. P., *Proc. Roy. Soc.* (*London*), **117A**, 600 (1928).
(9) THOMSON, G. P., *ibid.*, **119A**, 651 (1928).
(10) RUPP, E., *Ann. Physik*, (4), **85**, 981 (1928).
(11) RUPP, E., *Z. Physik*, **52**, 8 (1929); *Naturwissenschaften*, **16**, 656 (1928).
(12) WORSNOP, B. L., *Nature*, **123**, 164 (1929).
(13) WORSNOP, B. L., *Proc. Phys. Soc.* (*London*), **40**, 281 (1928).
(14) KIKUCHI, S., *Proc. Imp. Acad.* (*Tokyo*), **4**, 271, 275, 354, 471 (1928); *Japan. J. Physics*, **5**, 83 (1928).
(15) PONTE, M., *Compt. rend.*, **188**, 244 (1929).
(16) PONTE, M., *ibid.*, **188**, 909 (1929).
(17) PONTE, M., *Ann. phys.*, (10), **13**, 395 (1930).
(18) KIRCHNER, F., *Physik. Z.*, **31**, 772, 1025 (1930); *Naturwissenschaften*, **18**, 706, 707 (1930).
(19) DAUVILLIER, A., *Compt. rend.*, **191**, 708 (1930); *Nature*, **125**, 50 (1930).
(20) MARK, H. AND R. WIERL, *Naturwissenschaften*, **18**, 205, 778 (1930).
(21) MARK, H. AND R. WIERL, *Z. Elektrochem.*, **36**, 675 (1930).
(22) WIERL, R., "Leipziger Vortrage," Verlag von S. Hirzel, Leipzig, **1930**.
(23) THOMSON, G. P. AND C. G. FRASER, *Proc. Roy. Soc.* (*London*), **128A**, 641 (1930).
(24) BRAGG, W. L. AND J. A. DARBYSHIRE, *Trans. Faraday Soc.*, **28**, 522 (1932).
(25) GERMER, L. H., *Rev. Sci. Instruments*, **6**, 138 (1935).
(26) DARBYSHIRE, J. A. AND E. R. COOPER, *J. Sci. Instruments*, **12**, 10 (1935).
(27) REID, A., *Proc. Roy. Soc.* (*London.*), **119A**, 663 (1928).
(28) YAMAGUTI, T., *Proc. Phys. Math. Soc. Japan*, **16**, 95 (1934).
(29) TRILLAT, J. J. AND TH. V. HIRSCH, *J. phys. radium*, (7), **3**, 185 (1932).
(30) MORGAN, R. AND N. SMITH, *Rev. Sci. Instruments*, **6**, 316 (1935).
(31) FINCH, G. I. AND A. G. QUARRELL, *Proc. Roy. Soc.* (*London*), **141A**, 398 (1933).
(32) FINCH, G. I. AND A. G. QUARRELL, *ibid.*, **46**, 148 (1934).
(33) FINCH, G. I. AND A. G. QUARRELL, *Nature*, **131**, 842 (1933); *ibid.*, **133**, 758 (1934).
(34) LEBEDEFF, A. A., *ibid.*, **128**, 491 (1931).
(35) HUGHES, J. V., *Phil. Mag.*, **19**, 129 (1935).
(36) ARNOT, F. L., *Proc. Roy. Soc.* (*London*), **130A**, 655 (1931); *Nature*, **130**, 438 (1932).
(37) BRAUNE, H. AND S. KONKE, *Z. physik. Chem.*, **B21**, 297 (1933).
(38) DORNTE, R. W., *J. Am. Chem. Soc.*, **55**, 4126 (1933).
(39) DORNTE, R. W., *J. Chem. Phys.*, **1**, 566 (1933).
(40) HENDRICKS, S. B., L. R. MAXWELL, V. L. MOSLEY, AND M. E. JEFFERSON, *ibid.*, **1**, 549 (1933).
(41) DE LASZLO, H., *Proc. Roy. Soc.* (*London*), **146A**, 672 (1934).
(42) BORN, M., *Z. Physik*, **37**, 863 (1926); **38**, 803 (1926).
(43) MOTT, N. F., *Proc. Roy. Soc.* (*London*), **127A**, 658 (1930); *Proc. Cambridge Phil. Soc.*, **25**, 304 (1929).
(44) DYMOND, E. G. AND E. E. WATSON, *Proc. Roy. Soc.* (*London*), **122A**, 571 (1929).
(45) BULLARD, E. C. AND H. S. W. MASSEY, *ibid.*, **130A**, 579 (1931); *ibid.*, **133A**, 637 (1931).
(46) ARNOT, F. L., *ibid.*, **125A**, 660 (1929); *ibid.*, **129A**, 361 (1930); *ibid.*, **133A**, 615 (1931); *ibid.*, **140A**, 334 (1933).
(47) FAXEN, H. AND J. HOLTSMARK, *Z. Physik*, **45**, 307 (1927).
(48) THOMSON, G. P., *Proc. Roy. Soc.* (*London*), **125A**, 352 (1929).
(49) MARK, H. AND R. WIERL, *Z. Physik*, **60**, 741 (1930).
(50) DEBYE, P., *Ann. Physik*, **46**, 809 (1915).
(51) MASSEY, H. S. W., *Proc. Roy. Soc.* (*London*), **127A**, 666 (1930); *ibid.*, **129A**, 616 (1930).
(52) BETHE, H., *Ann. Physik*, (4), **87**, 55 (1928); *ibid.*, (5), **5**, 325 (1930).
(53) WIERL, R., *ibid.*, (5), **8**, 521 (1931).
(54) PAULING, L. AND L. O. BROCKWAY, *J. Chem. Phys.*, **2**, 867 (1934).
(55) MORSE, PH. M., *Physik. Z.*, **33**, 443 (1932).
(56) BEWILOGUA, L., *ibid.*, **33**, 688 (1932).
(57) DE LASZLO, H., *Nature*, **131**, 803 (1933).
(58) WIERL, R., *Ann. Physik*, **13**, 453 (1932).
(59) COSSLETT, V. E., *Trans. Faraday Soc.*, **30**, 981 (1934).
(60) ARNOT, F. L., *Proc. Roy. Soc.* (*London*), **144A**, 360 (1934).
(61) SUTTON, L. E. AND L. O. BROCKWAY, *J. Am. Chem. Soc.*, **57**, 473 (1935).
(62) BRU, L., *Anales soc. españ. fis. quim.*, **31**, 115 (1933).
(63) WIERL, R., *Physik. Z.*, **31**, 366 (1930).
(64) BERGMANN, E. AND L. ENGEL, *ibid.*, **32**, 263 (1931).
(65) BROCKWAY, L. O. AND L. PAULING, *Proc. Nat. Acad. Sci.*, **19**, 68 (1933).
(66) BROCKWAY, L. O. AND F. T. WALL, *J. Am. Chem. Soc.*, **56**, 2373 (1934).
(67) BRU, L., *Anales soc. españ. fis. quim.*, **30**, 438 (1932).
(68) PAULING, L. AND L. O. BROCKWAY, *Proc. Nat. Acad. Sci.*, **20**, 336 (1934).
(69) HENGSTENBERG, J. AND L. BRU, *Anales soc. españ. fis. quim.*, **30**, 341 (1932).
(70) BROCKWAY, L. O. AND L. PAULING, *Proc. Nat. Acad. Sci.*, **19**, 860 (1933).
(71) BROCKWAY, L. O., *ibid.*, **19**, 868 (1933).
(72) CARPENTER, D. C. AND L. O. BROCKWAY, *J. Am. Chem. Soc.*, **58**, 1270 (1936).
(73) MAXWELL, L. R., V. M. MOSLEY, AND L. S. DEMING, *J. Chem. Phys.*, **2**, 331 (1934).
(74) WIERL, R., *Physik. Z.*, **31**, 1028 (1930).
(75) BROCKWAY, L. O. AND H. O. JENKINS, *J. Am. Chem. Soc.*, **58**, 2036 (1936).

(76) PAULING, L. AND L. O. BROCKWAY, *J. Am. Chem. Soc.*, **59**, 13 (1937).
(77) ECKART, C., *Proc. Nat. Acad. Sci.*, **13**, 460 (1927).
(78) DAVISSON, C. AND L. H. GERMER, *ibid.*, **14**, 619 (1928).
(79) RUPP, E., *Ann. Physik*, (5), **1**, 773 (1929); *ibid.*, (5), **1**, 801 (1929).
(80) FARNSWORTH, H. E., *Phys. Rev.*, **40**, 684 (1932); *ibid.*, **43**, 900 (1933).
(81) DAMES, W., *Ann. Physik*, **12**, 185 (1932).
(82) EHRENBERG, W., *Phil. Mag.*, **18**, 878 (1934).
(83) SHINOHARA, K., *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **18**, 315 (1932).
(84) YAMAGUTI, T., *Proc. Math. Phys. Soc. Japan*, **17**, 58 (1935).
(85) TILLMAN, J. R., *Phil. Mag.*, **18**, 656 (1934).
(86) VON LAUE, M. AND E. RUPP, *Ann. Physik*, (5), **4**, 1097 (1930).
(87) FARNSWORTH, H. E., *Phys. Rev.*, **34**, 679 (1929); *Nature*, **123**, 941 (1929).
(88) FINCH, G. I. AND A. G. QUARRELL, *Nature*, **135**, 183 (1935).
(89) GERMER, L. H., *Phys. Rev.*, **44**, 1012 (1933).
(90) BRAGG, W. L., *Nature*, **124**, 125 (1929).
(91) DARBYSHIRE, J. A., *Z. Krist.*, **86**, 313 (1933).
(92) NISHIKAWA, S. AND S. KIKUCHI, *Nature*, **122**, 726 (1928).
(93) EMSLIE, A. G., *ibid.*, **123**, 977 (1929).
(94) GERMER, L. H., *Phys. Rev.*, **50**, 659 (1936).
(95) HOPKINS, H. G., *Phil. Mag.*, **21**, 820 (1936).
(96) KIRCHNER, F. AND H. RAETHER, *Physik. Z.*, **33**, 510 (1932).
(97) THOMSON, G. P., *Proc. Roy. Soc. (London)*, **133A**, 1 (1931); *Phil. Mag.*, **18**, 640 (1934).
(98) EMSLIE, A. G., *Phys. Rev.*, **45**, 43 (1934).
(99) TILLMAN, J. R., *Phil. Mag.*, **19**, 485 (1935).
(100) FINCH, G. I., A. G. QUARRELL, AND H. WILMAN, *Trans. Faraday Soc.*, **31**, 1051 (1935).
(101) DEUBNER, A., *Ann. Physik*, (5), **20**, 449 (1934).
(102) IRONSIDE, R., *Proc. Roy. Soc. (London)*, **119A**, 668 (1928).
(103) PRESTON, G. D. AND L. L. BIRCUMSHAW, *Phil. Mag.*, **21**, 713 (1936).
(104) DIXIT, K. R., *ibid.*, **16**, 1049 (1933).
(105) THOMSON, G. P., *Proc. Roy. Soc. (London)*, **128A**, 649 (1930).
(106) LASSEN, H., *Physik. Z.*, **35**, 172 (1934); LASSEN AND L. BRUCK, *Ann. Physik*, (5), **22**, 65 (1935).
(107) BRUCK, L., *Ann. Physik*, (5), **26**, 233 (1936).
(108) PRINS, J. A., *Z. Krist.*, **86**, 301 (1933).
(109) RICHARDS, D. A., *Phil. Mag.*, **16**, 778 (1933).
(110) TRILLAT, J. J. AND H. MOTZ, *Ann. Phys.*, (11), **4**, 273 (1935).
(111) DARBYSHIRE, J. A. AND E. R. COOPER, *Trans. Faraday Soc.*, **30**, 1038 (1934).
(112) EVANS, U. R., *J. Chem. Soc.*, **1927**, 1020; EVANS, U. R. AND J. STOCKDALE, *ibid.*, **1929**, 2651.
(113) DARBYSHIRE, J. A., *Trans. Faraday Soc.*, **27**, 675 (1931).
(114) SMITH, N., *J. Am. Chem. Soc.*, **58**, 173 (1936).
(115) YEARIAN, H. J., *Phys. Rev.*, **48**, 631 (1935).
(116) PRESTON, G. D., *Phil. Mag.*, **17**, 466 (1934).
(117) MURISON, C. A., *ibid.*, **17**, 96 (1934).
(118) VERWEY, E. J. W., *Z. Krist.*, **91**, 317 (1935).
(119) CATES, J., *Trans. Faraday Soc.*, **29**, 817 (1933).
(120) MONGAN, CH., *Helv. Phys. Acta*, **5**, 341 (1932).
(121) TRENDELENBURG, F., *Naturwissenschaften*, **20**, 655 (1932); *ibid.*, **21**, 173 (1933).
(122) BOERSCH, H. AND L. MEYER, *Z. physik. Chem.*, **29B**, 59 (1935).
(123) TRILLAT, J. J., *Kolloid-Z.*, **69**, 378 (1934).
(124) TRILLAT, J. J., *Chimie & industrie* (special no.), 175 (1934); *J. phys. radium*, (7), **4**, 38 (1933).
(125) TRILLAT, J. J. AND TH. V. HIRSCH, *Compt. rend.*, **195**, 215 (1932).
(126) MURISON, C. A., *Phil. Mag.*, **17**, 201 (1934).
(127) NELSON, H. R., *Phys. Rev.*, **44**, 717 (1933).
(128) STORKS, K. H. AND L. H. GERMER, *J. Chem. Phys.*, **5**, 131 (1937).
(129) JONES, E. T., *Phil. Mag.*, **16**, 793, 953 (1933); *ibid.*, **18**, 291 (1934).
(130) TRILLAT, J. J., *Compt. rend.*, **198**, 1025 (1934).
(131) TRILLAT, J. J. AND H. MOTZ, *ibid.*, **198**, 2147 (1934).
(132) RAETHER, H., *Z. Physik*, **86**, 82 (1933).
(133) FRENCH, R. C., *Proc. Roy. Soc. (London)*, **140A**, 637 (1933).
(134) DARBYSHIRE, J. A. AND K. R. DIXIT, *Phil. Mag.*, **16**, 961 (1933).
(135) GERMER, L. H., *Phys. Rev.*, **43**, 724 (1933).
(136) FINCH, G. I., A. G. QUARRELL, AND J. S. ROEBUCK, *Proc. Roy. Soc. (London)*, **145A**, 676 (1934).
(137) BATES, L. F., *Science Progress*, **30**, 82 (1935); *ibid.*, **24**, 196 (1929).
(138) JENKINS, R. O., *Phil. Mag.*, **17**, 457 (1934).
(139) ANDREWS, L. T., *Trans. Faraday Soc.*, **32**, 607 (1936).
(140) MAXWELL, L. R., *Phys. Rev.*, **44**, 73 (1933).
(141) GERMER, L. H., *Z. Physik*, **54**, 408 (1929).
(142) RUPP, E., *Ann. Physik*, (5), **5**, 453 (1930).
(143) RUPP, E. AND E. SCHMID, *Naturwissenschaften*, **18**, 459 (1930).
(144) BOAS, W. AND E. RUPP, *Ann. Physik*, (5), **13**, 1 (1932).
(145) RUPP, E., *Kolloid-Z.*, **69**, 369 (1934).
(146) VON LAUE, M., *Z. Krist.*, **84**, 1 (1932).
(147) BRILL, R., *Kolloid-Z.*, **69**, 301 (1934).
(148) ROLLIER, M. A., S. B. HENDRICKS, AND L. R. MAXWELL, *J. Chem. Phys.*, **4**, 648 (1936).
(149) CLARK, G. L. AND E. WOLTHUIS, *J. Applied Phys.*, **8**, 630 (1937).

On the WRITING *of* CHEMICAL EQUATIONS*

ALBERT L. JACOBS†

Pittsburgh, Pennsylvania

IN THE great strides of advancing chemstry—both pure and applied—attention to the lowly equation seems to have been overlooked even though it is one of the chemists' most useful and convenient tools. From a time whence the memory of living man runneth not to the contrary, equations have been written in the same old way, conveying more or less information to a favored few, but being practically, or entirely, meaningless to the beginning student, and even to many of those versed in other scientific fields.

* Patent pending.
† Chemical and metallurgical patent lawyer.

Something should be done about this. I propose to make a start. If, by what follows, I can focus some well-merited attention on this subject and provoke a discussion by or worth-while suggestion from interested readers, I will be gratified and thankful in having made some slight return to the chemistry which has done far more for me.

Since the present proposal is particularly directed to the student just beginning the study of chemistry, I ask indulgence of those to whom some of the present statements will seem elementary or even puerile.

Generally, after a brief historical glance at chemistry the teacher or textbook illustrates and explains the facts and concepts of chemistry by the use of equations and formulas. The real and full meaning of even such a simple equation as

$$NaOH + HCl = NaCl + H_2O$$

is, however, not readily apparent to and understood by the beginning student. If and when the student is told that one molecule of sodium hydroxide, which is composed of one sodium atom and one hydroxyl group, combines with one molecule of hydrochloric acid, which is composed of one chlorine atom and one hydrogen atom, to form one molecule of sodium chloride and one molecule of water the full import of the equation is not even then presented. It must be pointed out that in connection with the NaOH the O and H act together as a unit or element and that NaOH therefore subdivides for reacting purposes into Na and OH and not otherwise; that HCl subdivides into H and Cl and that the Na of the NaOH unites with the Cl of the HCl to form NaCl.

While the problem in a simple equation is not difficult the more complex the reaction the more involved and cumbersome the explanation becomes.

Would it not be convenient and highly useful to all concerned if all this information and explanation could be graphically or visually indicated in the equation itself by a very simple change in the manner of writing the same? The writer believes that the whole story can be told by writing the above reaction thus:

$$NaOH + HCl = NaCl + H_2O, \text{ or}$$
$$\mathbf{NaOH + HCl = NaCl + H_2O}$$

By merely changing the style of type, as above, the equation visually indicates how the reactants on the left-hand side of the equation subdivide for combining purposes to form the products on the right-hand side of the equation. It also shows which portions of the reactants combine and which products are therefrom formed. In short, the equation visually or graphically represents its course and tells exactly what happens. This "shorthand" explanation will save wear and tear on the student and will prevent the discouragement of students and others in trying to master chemistry.

The proposal is not limited to varying the type or style but may be indicated by using different colors or by adding simple geometrical designations; *e. g.*,

$$\underline{NaOH} + \overline{HCl} = \underline{NaCl} + H_2O \text{ or}$$
$$\boxed{Na}OH + H\boxed{Cl} = \boxed{\overline{NaCl}} + H_2O$$

Organic reactions lend themselves well to this proposal, due to the frequent custom of writing organic compounds in expanded form showing the linkages or bonds therein. For example, in conventional manner the hydrolysis of glyceryl trichlorhydrine to form glycerine and hydrochloric acid is written:

$$C_3H_5Cl_3 + 3H_2O = C_3H_5(OH)_3 + 3HCl$$

Contrast that equation with the same thing written thus in accordance with the present proposal:

$$\begin{array}{l} CH_2Cl \\ | \\ CHCl \\ | \\ CH_2Cl \end{array} + 3HOH = \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3HCl$$

Don't you think that the latter is more informatory and helpful than the former?

The proposed manner of re-writing chemical reactions would seem to have some advantages. The writer submitted to a person with little or no knowledge of chemical reactions the following two equations in the order set forth on different slips of paper:

(*A*) $SnS_2 + 4HCl = SnCl_4 + 2H_2S$ (conventionally written)
(*B*) $\boxed{Sn}S_2 + 4H\boxed{Cl} = \boxed{SnCl_4} + 2H_2S$ (new proposal)

Believe, if you will, that (*B*) conveyed much more meaning than (*A*) and that whereas the experimentee could give little or no explanation of (*A*) he could give considerably more about (*B*) and yet the above reactions were deliberately chosen for the test because they have perhaps a minimum of difference between them.

The proposal here set forth is applicable to mono- or polyatomic equations and where three, four, or more products are formed, two or more, as required, of the various forms of the proposal may be utilized.

To sum up, an equation written or reproduced in accordance with this proposal visually indicates the whole story on its face. It shows how the reactants subdivide, which parts thereof combine to form the products and each product on the right-hand side of the equation is visually and graphically distinct from other products. The products and their constituent parts are indicated in the same manner, but in a form distinct from any other product and its constituents or reactants.

To the profession and those interested the foregoing is submitted. Discussion or criticism is invited.

The METAL CARBONYLS*

V. PHYSIOLOGICAL PROPERTIES. VI. DERIVATIVES

WM. E. TROUT, JR.

Mary Baldwin College, Staunton, Virginia

V. PHYSIOLOGICAL PROPERTIES

THE unusually poisonous nature of nickel carbonyl introduces a considerable hazard into its study and application. The toxic nature of this compound offered a serious problem in the development of the Mond Nickel Process. Although a study of the toxicology of nickel carbonyl was made as early as 1890 by McKendrick and Snodgrass (*64*), and all precautions were taken by the Mond Nickel Company to avoid the poisoning of its employees, a bad accident subsequently took place in which ten men were poisoned, two of whom did not recover. Immediately Drs. Mosso and Armit were employed to study the problem anew, and their findings and suggestions (*65*) have enabled the Company to reduce accidents and poisoning to a minimum.

Obviously, the danger is just as great among chemists who are investigating the antiknock properties of the metal carbonyls. Only a few years ago in Dallas, Texas, a chemist, who was studying the antiknock properties of nickel carbonyl, poured the substance from one vessel to another and inhaled enough of the carbonyl to produce death after seven days of illness (*66*).

Although iron pentacarbonyl is not quite so toxic, its action is very similar to that of nickel carbonyl, and the discussion which follows, although confined largely to nickel carbonyl, will serve with slight modifications to describe the physiological effects of iron pentacarbonyl. Little is known concerning the toxicology of the remaining carbonyls.

Armit (*65*) has studied the toxic doses of the carbonyls in some detail. The subject of most concern to the worker, however, is the quantity of the carbonyl which makes air dangerous to breathe. The study of this problem is made more difficult by the ready dissociation of the carbonyl into nickel and carbon monoxide, as well as by the fact that industrial gases usually contain in addition to the carbonyl large quantities of carbon monoxide.

In their early studies of this subject, McKendrick and Snodgrass (*64*) concluded that 0.5 per cent. of nickel carbonyl vapor was necessary to make the air dangerous. However, this figure seems to be too high, for Haldane (*67*) has shown that as little as 0.05 per cent. of carbon monoxide in air produces disturbing symptoms which are appreciable even during rest. The toxicity of nickel carbonyl has been shown to be at least five times as great as that of carbon monoxide.

Armit (*65*) found that a rabbit was killed by one hour's exposure to air containing only 0.018 volume per cent. of nickel carbonyl. He determined the percentage of the carbonyl in the air directly by drawing the filtered air through aqua regia (which formed nickel salt and liberated carbon monoxide), evaporating the resulting solution to dryness, and determining the nickel in the residue with dimethyl glyoxime.

FIGURE 3.—EFFECTS OF NICKEL CARBONYL ON THE BRAIN TISSUES. DEGENERATIVE CHANGES IN THE GANGLION CELLS, AND NEUROPHAGIA AT THE BASE OF THE BRAIN IN NICKEL CARBONYL POISONING. (UNDER HIGH POWER. CRESYL VIOLET STAIN.) (Courtesy of the *Journal of the American Medical Association*)

The toxicity of cobalt tetracarbonyl, $Co_2(CO)_8$, was also studied by Armit (*68*). He found that 15 milligrams of cobalt per kilogram of body weight were required to kill a rabbit. However, the vapor pressure of cobalt tetracarbonyl is very small, and this fact was used by Armit to predict the comparative harmlessness of the vapor of this carbonyl. He assumed that only fifty per cent. of the carbonyl which was taken into the lungs was actually absorbed. The remainder was be-

* This is the third of a series of four articles concerning the metal carbonyls. The author reserves all rights to these articles.

lieved to be exhaled. In support of this assumption he pointed to the similar absorption of nickel carbonyl, iron pentacarbonyl, carbon monoxide, and some other gases. On the basis of this assumption and the known vapor pressure of cobalt carbonyl, Armit showed that a rabbit, in air which is saturated with the carbonyl, should absorb in the course of two hours only 1.8 cc. of the vapor of the carbonyl—a negligible amount. Experiments supported his prediction that the vapor pressure of

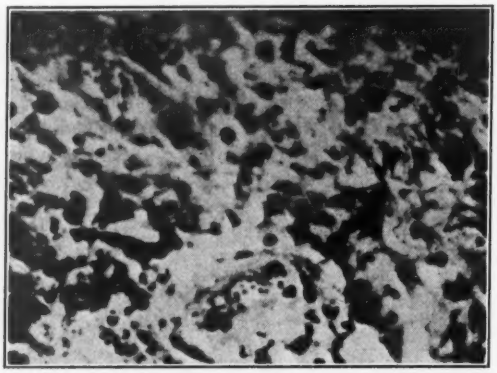


FIGURE 4.—EFFECT OF NICKEL CARBONYL ON LUNG TISSUES. DISINTEGRATION, FUSION, AND PROLIFERATION OF ALVEOLAR EPITHELIUM IN THE LUNGS OF A VICTIM OF NICKEL CARBONYL POISONING. (UNDER HIGH POWER. HEMATOXYLIN AND EOSIN STAIN.) (Courtesy of the *Journal of the American Medical Association*)

cobalt tetracarbonyl is so small and the dissociability of the compound so marked that it is unlikely that it will produce acute poisoning. Nothing was said concerning the effects of continued exposure to the carbonyl.

The symptoms (*67*) manifested immediately after exposure to the fumes of the nickel carbonyl include a feeling of giddiness, a throbbing headache, nausea, and occasionally vomiting. The patient may develop an unsteady gait. When carbon monoxide is mixed with gases containing nickel carbonyl—a frequent situation in industry—the patient may become unconscious. On the other hand, if the amount of nickel carbonyl in the air is very small, exposure of the worker for a long period may result only in a throbbing frontal headache.

These symptoms may disappear rather quickly and the patient may even be considered well enough to return to work. This "latent period," however, is often followed by remote symptoms, the most marked of which are dyspnoea (difficult or labored breathing) and pain in the middle of the chest on a line with the ends of the second, third, and fourth ribs. The degree of blueness of the lips and ears indicates the relative seriousness of the case. The patient's skin is pale, his forehead cold and clammy, and his general expression one of anxiety. The pulse increases in frequency and volume at first but may later become "thready." The temperature is normal during the first days, but rises in severe cases as the illness progresses. It is said that there is never any clinical evidence of organic damage to the central nervous system. A good diagnostic symptom is the presence of a trace of nickel in the urine collected during the first forty-eight hours. The physician generally analyzes 5 cc. of blood for nickel and carbon monoxide, using a spectroscopic test for the presence of carboxyhemoglobin formed by the action of liberated carbon monoxide in the blood.

The behavior of nickel carbonyl in the tissues is not entirely agreed upon. Armit (*65*) believed that the immediate symptoms were due to the action of the carbon monoxide liberated by the decomposition of the carbonyl in the blood. The quantity of carbon monoxide formed, however, is usually too small to be considered of much importance. Furthermore, the absence of nickel in the sputum and lungs of patients suggests that little decomposition takes place here. In support of this view, Haldane (*67*) found no carboxyhemoglobin in mice which died of nickel carbonyl poisoning. Amor suggests that most or all of the nickel carbonyl goes through the epithelium of the lung undecomposed, nevertheless producing much damage in that tissue. The presence of nickel in the liver and in the urine suggests that the carbonyl enters the blood stream unchanged.

The changes in the central nervous system are much more serious than those of carbon monoxide poisoning. Sir Frederick Mott (*67*) examined the brains in two fatal cases and found the covering of the brain to be rusty in color. Fine hemorrhages could be detected throughout the hemispheres, especially in the subcortical white matter. The chromatin was altered in the cells of the cerebral cortex and the cardio-respiratory centers of the medulla. Strangely enough, the symmetrical areas of softening which accompany carbon monoxide poisoning were not found.

Treatment of nickel carbonyl poisoning depends upon the severity of the case, and also on the degree of asphyxia, which may or may not indicate complication of the case by carbon monoxide poisoning. It need hardly be said that a physician should be called immediately.

For failure of respiration, a stimulant of this function should be used. Amor recommends $^{3}/_{20}$ grain of α-lobeline (Ingelhaim). For failure of heart action, he recommends 1 cc. of cardiazol or 0.01 grain of digitalin. If needed, a mixture of ninety-five per cent. oxygen and five per cent. carbon dioxide may be administered, preferably warm. The patient should be kept warm under any circumstance, and should not be taken out into the open if this change will chill him. The emergency treatment should be followed by absolute rest in order to relieve the heart and lungs of undue strain. The degree of dyspnoea should be the governing factor in deciding the time of return to work, and the kind of work to be done. Amor states that all patients on record who recovered from nickel carbonyl poisoning have returned to work.

Substantiation of many points made by Amor is found in the case reported by Brandes (*66*) and mentioned above. The symptoms and the autopsy were in

fairly good agreement. Some of the details, however, appear to warrant further study of the pathology of poisoning by nickel carbonyl. It is interesting to know that several associates of the patient were exposed to smaller doses of the nickel carbonyl at the same time that he inhaled a fatal quantity. These men suffered mild attacks of dyspnoea, but they quickly and completely recovered.

It is hoped that this brief discussion will convince those who wish to study the carbonyls that safety measures are necessary. The precautions are not, however, greater than those taken every day by many chemists. A well-ventilated hood should always be used in experiments with the carbonyls. The compounds should be kept in strong glass or steel containers, preferably under carbon dioxide or nitrogen. In the industry, leaks should be tested for constantly. The bright yellow luminosity of the flame of nickel carbonyl conveniently serves to indicate leaks. One part of nickel carbonyl in 80,000 may be detected in this manner. Repairmen in the Mond Nickel Company wear compressed air masks when there is danger of exposure.

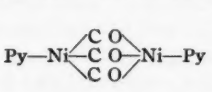
VI. DERIVATIVES

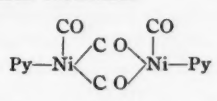
Addition and Substitution.—In view of the generally accepted characterization of the metal carbonyls one would expect to find derivatives in which the carbon monoxide is replaced by other groups. A large number of such compounds have been prepared. Although some of the compounds cannot be included accurately in either of these, the derivatives are generally of two types; addition compounds and substitution compounds.

The addition compounds are of the type represented by $Fe(CO)_5X_2$, where X represents a halogen atom. The substitution compounds may be represented by $Fe(CO)_4X$. Few of the compounds are salt-like. Reihlen's (*69*) $[Fe(CO)_3SC_2H_5]_2$ is an exception to this rule.

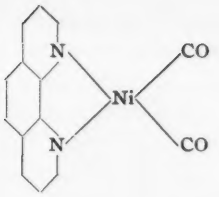
To Walter Hieber and his colleagues (*70*) goes the credit for the preparation of most of these derivatives. Hock and Stuhlmann (*71*) prepared the mercury halide derivatives, and Mittasch (*62*) and Reihlen (*69*) each have made a contribution.

Although for many years it was thought that nickel carbonyl did not form any compounds in which only a part of its carbon monoxide was replaced, Hieber, Muhlbauer, and Ehmann (*72*), in 1932, prepared compounds in which the carbon monoxide was replaced in part by pyridine and orthophenanthroline. They obtained air-sensitive, deep brown compounds, represented as $Ni_2(CO)_4py$* and $Ni(CO)_2py$,* for which they suggested the following structural formulas.





With orthophenanthroline, $Ni(CO)_2$(phth†) was obtained.



Iron and cobalt carbonyls lend themselves much more readily to the formation of such compounds. More than fifty such derivatives of iron carbonyls have been reported. Half a dozen such compounds of cobalt have been prepared by Hieber and his co-workers (*72*). In this connection it is interesting to note that cobalt-ammino carbonyls have been patented as antiknocks (*73*). It would be beyond the scope of this

M. I. T. Photo Service

ARTHUR A. BLANCHARD (1876–)

A Bostonian, educated at Massachusetts Institute of Technology and at Leipzig, Dr. Blanchard has, since 1903, been a member of the faculty of Massachusetts Institute of Technology, where he is professor of chemistry. He has published several books and a number of journal articles in the field of inorganic chemistry. He has, for the past dozen years, displayed an active interest in the field of the metal carbonyls, to which he has made significant contributions.

* py = pyridine.
† phth = orthophenanthroline.

paper to discuss these compounds in the detail which they deserve. It must serve to list a few of them.

$Fe(CO)_5Cl_2$	$Fe(CO)_4Hg$	$Fe(CO)_3en_2$
$Fe(CO)_5Br_2$	$Fe(CO)_4Hg_2Cl_2$	$Fe(CO)_3py$
$Fe(CO)_4Cl_2$	$Fe(CO)_3NH_3$	$Fe(CO)_3(py)_2$(indigo)
$Fe(CO)_4I_2$	$Fe(CO)_3(NH_3)_2$	$Co_2(CO)_5(CH_3OH)$
$Fe(CO)(py)(CN)_2$	$Fe(CO)_2NH_3$	$Co_2(CO)_5(py)_4$
$Fe(CO)_3HgCl_2$	$Fe(CO)_3(CH_3OH)$	$Co(CO)_3$(phth)

Whereas substitution in nickel carbonyl takes place at room temperature (although slowly), and in iron carbonyl at 80°, substitution in the hexacarbonyls takes place only under extreme conditions (*63*), such as refluxing at 116° or heating in a sealed tube at temperatures from 140° to 200°. By these procedures $Cr(CO)_4py$, $Cr(CO)_7py_5$, and $Cr(CO)_3py_3$ have been prepared, as well as $Mo(CO)_3py_2$, $Cr_2(CO)_6py_3$, $Cr(CO)_4$(phth), and $Mo(CO)_3$(phth)(py).

Although the pyridine derivatives of the iron group are pyrophoric, most of the derivatives of the hexacarbonyls are stable in air.

Perhaps the most interesting of the derivatives of the metal carbonyls are the nitrosyl carbonyls (also called nitroso carbonyls) and the carbonyl hydrides. Because of the interest which they have recently stimulated, we shall discuss these compounds in some detail.

Nitrosyl Carbonyls.—Soon after the discovery of nickel carbonyl, Marcellin Berthelot (*74*) passed nitric oxide into the vapor of this substance and observed the formation of blue fumes which settled slowly. A similar solid was formed in liquid nickel carbonyl. Berthelot characterized these solids as complex and did not study them further. Thirty years later, R. L. Mond and A. E. Wallis (*75*) attempted to determine the nature of these complex solids, but met with little success. They suggested the presence of $Ni(NO)_2$, but could not substantiate their view. They succeeded, however, in preparing by a similar procedure two volatile nitrosyl carbonyls, $Co(NO)(CO)_3$ and a compound which they thought to be $Fe(NO)\cdot 3Fe(CO)_5$, but which was later shown by Hieber and Anderson (*76*) to be $Fe(NO)_2(CO)_2$. Recently, Blanchard and his co-workers (*77*) have prepared these compounds by passing carbon monoxide and nitric oxide into sulfide, cyanide, or cysteine solutions of the appropriate metal salt.

By passing nitric oxide over cobalt tetracarbonyl at 40°, Mond and Wallis obtained a volatile, cherry-red, mobile liquid, stable under water, in which it is insoluble. Its solubility is similar to that of the true carbonyls; that is, it is miscible in all proportions with alcohol, benzene, ether, chloroform, etc. It distils in a current of inert gas at 50° to 60° with slight decomposition into the tricarbonyl and nitric oxide. Above 66° the compound slowly decomposes to liberate nitric oxide and to form the tricarbonyl, $Co_4(CO)_{12}$. The physical properties of the nitrosyl carbonyl are listed in Table 2.

The reaction by which cobalt nitrosyl carbonyl is prepared is regarded as one in which carbon monoxide is replaced by nitric oxide, according to the following equation.

$$\underset{\text{dimer}}{Co(CO)_4} + NO \longrightarrow Co(CO)_3NO + CO$$

The action of nitric oxide on the tricarbonyl of cobalt at 75° to 80° formed too small a quantity of the nitrosyl carbonyl to be collected.

Hieber and Anderson (*78*) prepared several derivatives of cobalt nitrosyl carbonyl and showed that in both the cobalt and the iron nitrosyl carbonyls, the carbon monoxide group could be substituted but not the nitric oxide group. They obtained the compounds $Co_2(CO)(NO)_2py_2$, $Co(CO)_2(NO)$(phth), and $Co(CO)$-(NO)(phth) by action of the complex forming organic compounds on the nitrosyl carbonyl.

During the course of this work, Hieber called attention to the fact that cobalt trinitrosyl, $Co(NO)_3$, was obtained. This compound had earlier been obtained in the laboratory of the I. G. Farbenindustrie A.-G., and recorded in German patents under the names of L. Schlecht, G. Hamprecht, and F. Spoun (*79*). They obtained this dark brown crystalline compound by treatment of finely divided cobalt with carbon monoxide and nitric oxide at 150° under atmospheric pressure. The compound may be sublimed *in vacuo* without decomposition. In mixtures containing more than fifteen per cent. nitric oxide, $Co(NO)_3$ was obtained. With five to fifteen per cent. nitric oxide in the mixtures, some $Co(CO)_3(NO)$ was formed.

TABLE 2

PROPERTIES OF THE NITROSYL CARBONYLS (*76*)

	$Co(CO)_3(NO)$	$Fe(CO)_2(NO)_2$
Molecular weight	173	172
Melting point	−11°	18.4°
Vapor pressure (20°)	91 mm.	20 mm.
Boiling point	78.6°	110° (extrapolated)
Specific gravity (20°)	1.47	1.56
Mol volume	117	110
Trouton's constant	22.6	24.0
Temperature at which decomposition is just detectable	55°	50°

Mond and Wallis (*75*) found that nitric oxide did not react with $Fe_2(CO)_9$ up to 60°. At 63°, however, slight reaction occurred and red beads of liquid appeared. At 70° to 85° reaction was regular and the solid enneacarbonyl gradually gave place to the red liquid.

The red liquid was further studied by Hieber and Anderson (*76*), who found the compound to form red crystals melting at 18.5°. By slow sublimation, shiny six-sided leaves of several millimeters thickness were obtained. As a result of the small heat of fusion, the liquid nitrosyl carbonyl, like various other carbonyls, is easily undercooled. The compound decomposes appreciably at 70°, is rapidly oxidized in air, and is decomposed rapidly by halogens.

Hieber and Anderson prepared several derivatives of this compound; $Fe(NO)_2$(phth), $Fe_2(NO)_4py_2$, Fe-$(NO)_2I$, and $(Fe(NO)_2)_x$. The last compound was not isolated in pure form.

By the vigorous action of liquid nitric oxide on iron pentacarbonyl in a sealed tube at 44° to 45° and subsequently cooling to −70°, Manchot and Enk (*80*)

obtained black needles, fuming in air, corresponding to the formula $Fe(NO)_4$.* These crystals burned with sparking in warm oxygen, formed $Fe(NO)SO_4$ in dilute sulfuric acid without liberation of hydrogen, and formed a red solution with concentrated sulfuric acid.

Manchot (*80, 81*), in 1929, undertook to study the replacement of carbon monoxide in complex compounds by nitric oxide. By the action of nitric oxide on iron pentacarbonyl in methyl alcohol, he obtained as one of the products, $Fe(NO)\cdot xCH_3OH$ (where x was about 2), a black, microcrystalline solid. Hieber and his co-workers (*78*) prepared $Fe(CO)_3(NO)(py)$ (uncertain) and $Fe_2(NO)_4I_3$. Reihlen (*82*) and his co-workers prepared compounds which they considered to be $Fe_2(NO)_2(CH_3O)_3(OH)$, and $Ni(NO)(OCH_3)(OH) + CH_3OH$. Many other nitrosyl compounds of complex nature, not closely related to the carbonyls, are known.

The explanation of the constitution of the nitrosyl compounds has roused much interest. Reihlen (*82*) regards them as derivatives of acids similar to hyponitrous acid, in accord with his views concerning the structure of the metal carbonyls. Reiff (*83*) interpreted the structure of cobalt tricarbonyl nitrosyl and also of cobalt trinitrosyl (which he predicted) in terms of the effective atomic number, extending Langmuir's (*52*) suggestion concerning the structure of nickel carbonyl and iron pentacarbonyl. It was suggested that nitric oxide contributed three electrons to the binding of the group to the metal atom, whereas carbon monoxide contributed two.

Sidgwick and Bailey (*51*) have reviewed the structure of the nitrosyl carbonyls and find only one explanation tenable, and that is in agreement with the suggestion of Reiff, that the nitrogen of the nitrosyl group contributes three electrons to the binding with the metal, forming both a coördinate link and a covalent link. They represent this as follows: M:N :::O: or $M^-—N^+\equiv O^+$.

The inert gas rule which was suggested as an explanation of the structure of the metal carbonyls and the equation representing the rule (see THIS JOURNAL, **14,** 577 (1937)) were extended by these authors to apply to the nitrosyl carbonyls. It is as follows, where "z" represents the number of nitrosyl groups in the molecule.

$$G - \frac{xm + 2y + 3z}{x} = x - 1$$

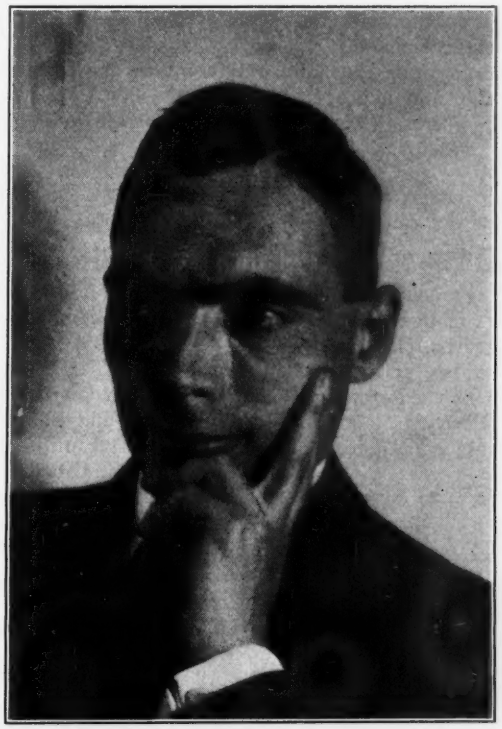
It is interesting to see that this rule applies to $Fe(CO)_2(NO)_2$, $Co(CO)_3(NO)$, $Co(NO)_3$, $Fe(NO)_2(phth)$, $Co(CO)(NO)(phth)$, and $Fe_2(NO)_4(py)_3$. It does not, however, apply to the compound $Fe(NO)_4$.

Carbonyl Hydrides.—Two compounds which very recently have interested investigators of the metal carbonyls are the unusual hydrides of iron and cobalt carbonyls, $Fe(CO)_4H_2$ and $Co(CO)_4H$.

In 1931, Hieber and Leutert (*84*) reported the formation of an unstable liquid by the action of bases on iron pentacarbonyl, which they represented by the equation

$$Fe(CO)_5 + 2OH^- \longrightarrow Fe(CO)_4H_2 + CO_3^=$$

They later (*85*) prepared the iron carbonyl hydride by the action of barium hydroxide or sodium methylate on iron pentacarbonyl, and by the action of acid on



HANS REIHLEN
PROFESSOR OF CHEMISTRY AT THE UNIVERSITY OF TÜBINGEN

complex derivatives of $Fe(CO)_4^-$ or $Fe(CO)_3^-$ radicals. They represented these reactions by the following equations.

$$Fe(CO)_5 + Ba(OH)_2 \longrightarrow Fe(CO)_4H_2 + BaCO_3$$
$$Fe(CO)_5 + CH_3ONa + H_2O \longrightarrow Fe(CO)_4H_2 + CH_3O\cdot CO\cdot ONa$$
$$Fe(CO)_4(en) + 8H^+ \longrightarrow Fe(CO)_4H_2 + Fe^{++} + 3(en2H)^{++}$$
$$3Fe(CO)_3 + 2H^+ \longrightarrow Fe(CO)_4H_2 + Fe(CO)_5 + Fe^{++}$$
$$2Fe(CO)_3 + 2H^+ \longrightarrow Fe(CO)_4H_2 + Fe^{++} + 2CO$$

$Fe(CO)_3$ represents the red iron tricarbonyl, which Hieber and his co-workers frequently mention, but which is apparently present only in the tricarbonyl complexes. It is said by them to decompose by disproportionation and to react with iron pentacarbonyl according to equations such as the following.

$$2Fe(CO)_3 \longrightarrow Fe(CO)_4 + Fe(CO)_2$$
$$Fe(CO)_3 + Fe(CO)_5 \longrightarrow 2Fe(CO)_4$$

The iron carbonyl hydride is difficult to purify and was obtained in colorless, pure form only after succes-

* Manchot and Manchot (*Z. anorg. Chem.*, **226,** 385 (1936)) have prepared an analogous compound of ruthenium, $Ru(NO)_5$; an unstable compound forming red, cubic crystals.

sive fractional distillation in a high vacuum. It forms colorless crystals melting at 70°.

The most striking property of the compound is perhaps its high degree of instability. It decomposes spontaneously, according to Hieber, in agreement with the following equation.

$$2Fe(CO)_4H_2 \longrightarrow Fe(CO)_5 + Fe(CO)_3 + 2H_2$$

The iron tricarbonyl which is formed decomposes as shown previously.

The hydride is wholly indifferent to dry hydrogen chloride and hydrogen bromide at −30°. In ether, iodine reacts in small amounts to liberate hydrogen.

$$Fe(CO)_4H_2 + I_2 \longrightarrow Fe(CO)_4I_2 + H_2$$

When larger amounts of iodine are present, hydrogen iodide is formed.

$$Fe(CO)_4H_2 + I_2 \longrightarrow Fe(CO)_4I_2 + 2HI$$

The compound reduces methylene blue, and also reduces manganese dioxide with the formation of iron tetracarbonyl.

Pyridine and orthophenanthroline stabilize the hydride by the formation of complex addition compounds.

As early as 1932, Hieber, Muhlbauer, and Ehmann (*86*), in a footnote, reported that investigations of the action of a base on cobalt carbonyl were in agreement with the existence of a hydrogen containing cobalt carbonyl, the stoichiometric composition of which was not yet proved, but which they suggested to be $Co(CO)_4H$.

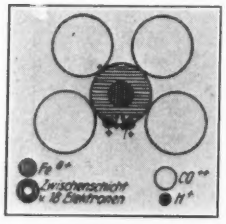


FIGURE 5.—A DIAGRAM ILLUSTRATING HIEBER'S CONCEPT OF IRON CARBONYL HYDRIDE $Fe(CO)_4H_2$. (Courtesy of the *Zeitschrift für anorganische und allgemeine Chemie*)

In 1934, Hieber (*87*) reported the preparation of this compound by several reactions and in 1936 (*88*) reported further studies. Schubert (*89*), in 1933, and Coleman and Blanchard (*90*), in 1936, reported the preparation of this compound by the action of carbon monoxide on an alkaline solution of cobalt chloride containing cysteine or tartrate. The methods of preparation are summarized in the reactions given by the investigators:

Hieber, *et al.*:

(Strong Bases)

$$3Co(CO)_4 + 2OH^- \longrightarrow \underset{\text{dimer}}{2HCo(CO)_4} + \underset{\text{polymer}}{Co(CO)_3} + CO_3^=$$

(Weak Bases)

$$3Co(CO)_4 + 2H_2O \longrightarrow 2HCo(CO)_4 + Co(CO)_4 + Co(OH)_2 + 4CO$$

$$2Co(CO)_3M + 2H^+ \longrightarrow Co^{++} + Co(CO)_4H + 2CO + {}^1/_2H_2 + M$$

(M = alcohol or ammine component)

Schubert:

$$CoCl_2 + 2HSRH\cdot HCl + 6KOH \longrightarrow K_2[Co(SR)_2] + 4KCl + 6H_2O$$

$$9K_2[Co(SR)_2] + 8CO + 2H_2O \longrightarrow 6K_3[Co(SR)_3] + 2H[Co(CO)_4]$$

$$K_3[Co(SR)_3] + 6CO + 7KOH \longrightarrow H[Co(CO)_4] + 2K_2CO_3 + 3K_2RS + 3H_2O$$

Hieber:

$$6CoCl_2 + 12K(Xa) + 5CO + M \longrightarrow Co_2(CO)_5\cdot M + 4Co(Xa)_2$$

(Xa = $C_2H_5O\cdot C(:S)\cdot S-$)

$$Co_2(CO)_5M + 2H^+ \longrightarrow HCo(CO_4) + Co^{++} + CO + {}^1/_2H_2 + M$$

$$2[Fe(CO)_4H]2Co(CO)_4 \longrightarrow 2Co(CO)_4H + Fe(CO)_4H_2 + 3Fe(CO)_4$$

The hydride forms pale yellow crystals melting at −26° to a dark yellow liquid. Cobalt tetracarbonyl hydride is much less stable than the corresponding iron derivative. As a consequence, the base used in its preparation must be ten times more dilute than that used in the formation of the iron compound. Because of this instability, the purification of the compound by high vacuum distillation must be carried out below −20°. Air must be carefully excluded.

Decomposition sets in at about −18°, liberating hydrogen and leaving pure crystalline cobalt tetracarbonyl

$$2HCo(CO)_4 \longrightarrow [Co(CO)_4]_2 + H_2$$

This reaction was used for analysis of the hydride.

Two opinions are held concerning the nature of the carbonyl hydrides. The first is that they are acids. Feigl (*91*), Schubert (*89*), and Blanchard (*90*) have regarded these compounds as acid in nature. Blanchard regards cobalt carbonyl hydride as an acid of greater strength than carbonic acid. In support of this view is the work of Schubert. He prepared what appear to be metal salts of the hydride, $Hg[Co(CO)_4]_2$, $Ag[Co(CO)_4]^1/_2H_2O$, $Ag[Co(CO)_4]2H_2O$, and he believed the potassium salt of the hydride, $K[Co(CO)_4]$, to be an intermediate compound in his method of preparation of the hydride.

Of interest in this connection are a number of compounds prepared by Feigl and by Hieber:

Feigl:

$[Fe(CO)_4][Cd(NH_3)_2]$ $[Fe(CO_4)H_2][Ni(NH_3)_6]$
$[Fe(CO)_4][Cd(py)_2]$ $[Fe(CO)_4]Cd$
$[Fe(CO)_4H_2][Fe(phth)_3]$

Hieber:

$[Co(CO)_4]_2[Ni(phth)_3]$ $[Fe(CO)_4H]_2[Ni(NH_3)_6]$
$[Co(CO)_4]_2[Co(phth)_3]$ $[Fe(CO)_4H]_2\cdot Ni(CO)_4$*
$[Co(CO)_4]_2[Ni(NH_3)_6]$ $[Fe(CO_4)H]_2\cdot Co(CO)_4$*

Feigl regards these compounds as evidence of the acid character of the carbonyl hydrides.

The second opinion concerning the nature of the

* It is suggested that the last two compounds of iron, called by K. Kraemer (*88*) "mixed carbonyls," should serve as sources of carbonyls according to the following equations, which take place quantitatively:

$$[Fe(CO)_4H]_2\cdot Ni(CO)_4 \longrightarrow Fe(CO)_4H_2 + Fe(CO)_4 + Ni(CO)_4\uparrow$$

$Fe(CO)_4 \rightarrow Fe(CO)_5$

$$2[Fe(CO)_4H]_2\cdot Co(CO)_4 \longrightarrow 2Co(CO)_4H + Fe(CO)_4H_2 + 3Fe(CO)_4$$

carbonyl hydrides was proposed by Hieber. In contrast to the preceding investigators, Hieber appears to regard the hydrogen atoms of the carbonyl hydrides as tightly bound to the metal atom where they act as "addition centers" to which other atoms and ions, such as nitrogen in pyridine and oxygen in hydroxyl radical, are bound. He supports his views with experimental evidence.

It will be evident that the study of the derivatives of the metal carbonyls, especially the carbonyl hydrides and the nitrosyl carbonyls, has thrown much light on the nature of these peculiar compounds. One investigator has said that the nature of the metal carbonyls is now known "without doubt." The few dissenting voices lead us to look forward with much interest to the future course of the studies of the metal carbonyls.

LITERATURE CITED

(64) McKENDRICK AND SNODGRASS, *Proc. Phil. Soc., Glasgow*, **22,** 204 (1890–91).
(65) ARMIT, *J. Hyg.*, **7,** 525 (1907); *ibid.*, **8,** 565 (1908).
(66) BRANDES, *J. Amer. Med. Assoc.*, **102,** 1204 (1934).
(67) AMOR, *J. Ind. Hyg.*, **14,** 216 (1932).
(68) ARMIT, *J. Hyg.*, **9,** 249 (1909).
(69) REIHLEN, v. FRIEDOLSHEIM, AND OSTWALD, *Ann.*, **465,** 72, 83 (1928).
(70) For the derivatives of iron carbonyls, see ABEGG, "Handbuch der anorganischen Chemie," Hirzel, Leipzig, **1930,** Vol. IV, 2 Bl, p. 451.
(71) HOCK AND STUHLMANN, *Ber.*, **61,** 2097 (1928); *ibid.*, **62,** 431, 2690 (1929).
(72) HIEBER, MUHLBAUER, AND EHMANN, *ibid.*, **65,** 1090 (1932).
(73) Standard Oil Co. of Calif., *U. S. Pat.*, 1,779,061.
(74) BERTHELOT, *Compt. rend.*, **112,** 1343 (1891); *Bull. soc. chim.*, **7–8,** 431, 434 (1892).
(75) MOND AND WALLIS, *J. Chem. Soc.*, **121,** 32 (1922).
(76) HIEBER AND ANDERSON, *Z. anorg. Chem.*, **208,** 238 (1932).
(77) BLANCHARD, ET AL., *J. Am. Chem. Soc.*, **56,** 826 (1934); *ibid.*, **58,** 2160 (1936).
(78) HIEBER AND ANDERSON, *Z. anorg. Chem.*, **211,** 132 (1933).
(79) *German Pats.*, 613,400; 613,401: *U. S. Pat.*, 1,992,637 (1935).
(80) MANCHOT AND ENK, *Ann.*, **470,** 275 (1929).
(81) MANCHOT AND GALL, *ibid.*, **470,** 271 (1929).
(82) REIHLEN, GRUHL, HESSLING, AND PFRENGLE, *ibid.*, **482,** 161 (1930).
(83) REIFF, *Z. anorg. Chem.*, **202,** 375 (1931).
(84) HIEBER AND LEUTERT, *Naturwissenschaften*, **19,** 360 (1931).
(85) HIEBER, ET AL., *Z. anorg. Chem.*, **204,** 145, 165 (1932); *ibid.*, **212,** 145 (1933); *Ber.*, **65,** 1092 (1932); *Z. Elektrochem.*, **40,** 158 (1934).
(86) HIEBER, MUHLBAUER, AND EHMANN, *Ber.*, **65,** 1090, 1092 (1932).
(87) HIEBER, *Z. Elektrochem.*, **40,** 158 (1934).
(88) HIEBER, *Z. angew. Chem.*, **49,** 463 (1936).
(89) SCHUBERT, *J. Am. Chem. Soc.*, **55,** 4563 (1933).
(90) COLEMAN AND BLANCHARD, *ibid.*, **58,** 2160 (1936).
(91) FEIGL AND KRUMHOLZ, *Monatsh.*, **59,** 314 (1932); *Z. anorg. Chem.*, **215,** 242 (1933).

A NEW DISTILLATION COLUMN*

E. H. PARKE

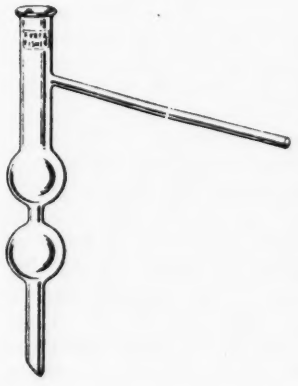
Oberlin College, Oberlin, Ohio

FOR some years there has been the criticism of the distillation columns of the two-bulb type shown in the catalogs in that they were unnecessarily large and cumbersome for convenience in the college laboratory.

About fifteen years ago the writer designed a distillation column which has been used in this laboratory ever since. This column was 21 mm. o.d., and 180 mm. overall. The upper bulb was 35 mm. outside diameter and the lower one 25 mm. o.d. The two were separated by a constriction 25 mm. long and 9 mm. o.d. The side tube, 150 mm. long and 6 mm. o.d. was sealed on to the column 35 mm. from its top.

This design has now been changed to the following. The new column is 220 mm. overall and 22 mm. o.d. Both bulbs are of the same diameter, *i. e.*, 35 mm. o.d. The upper bulb is 80 mm. from the top of the column and separated from the lower one by a constriction 20 mm. long and 10 mm. o.d. The side tube is sealed on to the column 40 mm. from its top, at a 70° angle to the lower column, and is 150 mm. long and 6 mm. o.d. The tip of the column is of the same diameter as the constriction between the bulbs and is 50 mm. long with the end ground to a 60° angle. This column will be found to be much more efficient than the larger ones in distilling small quantities of liquids.

While these columns were formerly of ordinary glass, it is preferable to make them of Pyrex in order to minimize breakage, although the initial cost is perhaps twice that of ordinary glass.



The walls of the bulbs should be as thick as the stock of the column will permit so that when glass beads or short pieces of glass tubing are used in the bulb, to facilitate fractionating, breakage is less likely to occur when they are dropped in.

* See Editor's Outlook.

RESEARCH PROBLEMS *for* SECONDARY SCHOOL PUPILS

VERNE R. ROSS

Technical High School, Springfield, Massachusetts

Simple problems within the scope of ability of high-school pupils are selected for investigation by the more intelligent pupils. The objective is not the production of finished research problems, but the development of the unusual pupil. Five case studies are given. These are typical of two types of problems—laboratory and library development. The work of these case studies was carried on several years ago and later achievement of the pupils observed. Their work in high school was a forerunner of later success in science or engineering.

✦ ✦ ✦ ✦ ✦ ✦

DURING the last quarter century the science of chemistry has been presented to thousands of pupils in the secondary schools of the nation. Although this science appeals to the interests of the great mass of boys and girls in a manner more or less satisfying to their curiosity, it is only occasionally that the individual appears to whom chemistry presents a great challenge. Such a pupil enters its study with an enthusiasm that, even in his high-school days, carries him to heights of achievement which in their perspective give him a view of the science and its possibilities. He is fired with an ambition to enter this field and find his life work.

The pupil of this description is usually of superior intelligence, and his personality is such that he is not satisfied with the ordinary and average achievement of his fellows. Mastering the essentials readily, he has a surplus of energy that may be directed into channels which will develop him into an individual who will attain distinction in adult life, and who will make original contributions to knowledge and human welfare. To the chemistry instructor is presented the challenge of inspiring such latent ability and developing these potential scientists so that they may take a place in that line which continues and develops knowledge.

It has been the good fortune of the author to have had contact, through many years of teaching experience, with several of these superior pupils and to have, in a measure, guided them into the great opportunities of chemical science and its related fields. This experience has been in Covina Union High School, located in one of the major citrus-producing districts of Southern California. Chemistry was taught in the junior year of high school, at which time potential talent was discovered. Nearly every year a limited number of outstanding pupils was discovered, and they were encouraged to begin the study of physics in their senior year. This subject was also taught by the author. The scientific interests of these pupils was so intense that they were willing to work on special problems before and after school hours and above and beyond the required curriculum. The laboratories were unusually well equipped by a sympathetic superintendent and school board, and furnished facilities for the investigation of simple problems.

In all projects of this nature the objective has not been the production of finished research problems in chemistry, but rather the development of the individual pupil. Starting with the native curiosity of the student, his superior intellectual endowment and his surplus energy we have made an attempt to utilize these factors of personality in the formation of a character and the production of an individual who can take a place worthy of his talents in the life of the world.

The community being primarily devoted to citriculture, many simple yet interesting problems are found in this industry or its related activities which are within the range of investigation of a superior high-school pupil. It is the duty of the instructor to lead the pupil to a discovery of these problems and inspire him to a pursuit of their study. Along with the development of a scientific attitude on the part of the pupils there have been isolated instances in which they have made scientific contributions of some value.

Illustrative of results obtained five typical case studies are selected from many that have been produced. During the progress of an individual problem, reference work has been encouraged and laboratory notebooks kept. The results of the work were always written in the form of a thesis, giving methods, data tables, illustrations and drawings, references cited, and bibliographies.

CASE I—"A STUDY OF SOAP POWDERS USED IN SPRAYING CITRUS TREES FOR BLACK SCALE CONTROL"

An early method for the control of black scale involved the use of soap powders as the active constituent of sprays. Occasionally damage resulted to

foliage and fruit. This study undertook a determination of the source of this damage. In an attack on the problem an analysis was made of three brands of soap powders determining moisture, free alkali, total alkali combined with fatty acid, alkali combined as carbonate, combined fatty acids, and insoluble matter. Standard solutions were prepared, titrations carried on, the analytical balance mastered and usual chemical manipulations used. In order to carry on the laboratory work and become familiar with the general aspects of the problem it was necessary to do much reference work from a library standpoint. From the compositions of the soaps as determined analytically it was possible to prepare solutions of their individual constituents comparable to concentrations used in commercial products. To determine which of these were harmful to foliage, controlled plots of young wheat and oat plants were sprayed. Sodium carbonate was found to be the harmful constituent.

This project was carried on during the school year 1914–15. The boy responsible for its prosecution was one of those outstanding individuals who are a joy to any teacher. On the completion of his high-school course he entered Pomona College where he received the A.B. and A.M. degrees. His graduate work involved a Ph.D. degree from Harvard University followed by a year of study in Germany. During all this time chemistry was his major. At present he is a professor of chemistry at a leading Pacific Coast university. Within recent weeks he has been recognized as one of the outstanding research men in the field of chemistry by being awarded $2500 from a famous scientific foundation for detailed research in a very definite field. Although he has published many papers giving the results of his chemical researches he has stated that this high-school problem was, in its limited way, as much of a research project as any of his later studies.

CASE II—"AN INVESTIGATION OF THE ACID-SOLID RATIO OF RIPENING ORANGES"

Oranges are legally ripe when the ratio of total acids (as citric) to total soluble solids is 1 to 8. This study undertook a determination of the rate of development of this ratio, along with the rate of growth of the orange. The laboratory work called for the preparation of standard solutions, the use of the analytical balance and the Brix hydrometer. The acid content of the fruit juice was determined by titration and the soluble solids by the hydrometer, and, as an occasional check, the use of a pycnometer. In the field work definite orange trees, both navel and valencia, were selected in a normal grove. On these trees individual oranges were labeled and their growth was determined by periodically measuring the circumference with a steel tape. Fruit from the immediate neighborhood of these marked samples was picked and the acid content and soluble solids determined. About two months' time was found to be required for the orange to mature after the color had begun to turn from green to yellow.

The fruit on the south side of the tree matured about three weeks in advance of that on the north side.

The boy responsible for this project was a brother of the one described in Case I. He did the work in the school year 1918-19. He attended Pomona College where he received the A.B. degree, went to Harvard for the Ph.D., and followed this with a year in Germany. At present he is a professor in a leading Western institution. In addition to his teaching duties he carries on an extensive research program and has many publications to his credit.

CASE III—"THE COMPOSITION OF AN ORANGE TREE"

The removal of the orange trees from a five-acre plot for the development of a new athletic field presented the opportunity of determining the relative proportions of fruit, leaves, wood, and roots in a tree. A mature tree seventeen feet tall was selected and all the leaves picked and weighed. The branches and trunk were cut, the stump and roots pulled, and each weighed. Leaf surface was determined by fitting samples of leaves into a two square foot pattern on a table top and thus determining the weight of a given area of leaf surface. The make-up of the tree was found to be eleven per cent. leaves, fifty-five per cent. wood, twenty-three per cent. roots, and eleven per cent. fruit. The entire leaf surface was calculated as 2333 square feet. To this point the work was largely mechanical. The laboratory aspects involved the determination of the per cent. of moisture, ash, and organic matter in the leaves, fruit, bark, wood, and roots, and qualitative tests which revealed the presence of twelve elements and radicals.

The boy who pursued this problem did it in the school year 1924-25. He was one of the few who did not go into science or engineering as a life work. He attended a professional school for two years and then entered business in his home community.

The advent of the Garvan Prize Essays in Chemistry offered to high-school students a reward of $20 in gold in each of six divisions for each state in the Union and six national prizes equivalent to $500 per annum and tuition in any standard university for four years. The preparation of these essays was largely from a library and reference standpoint and did not involve laboratory work. The rewards held out by this contest had a great appeal to students. The nature of the essays somewhat modified the activities of the science department of Covina Union High School in its attempts to utilize the energies of ambitious pupils. Laboratory work not being a part of the contest conditions, this phase of the activities was not pushed during the years the Garvan Contest was held. Several students wrote essays each year and the school was for five successive years represented by winners in the state contest and one took second place in a division of the national contest. Cases four and five are selected from these papers.

CASE IV—"THE DEVELOPMENT OF THE PHOTOGRAPHIC INDUSTRY"

The boy who treated this subject was an ardent amateur photographer and built his essay on his interest. He developed the topic from the historical side, illustrating the document with exhibits showing various stages in the growth of the industry. Through the paper the part that chemistry played was stressed. In the preparation of the paper a large volume of reference work was required and the boy went to original sources in many cases. The paper won first place in its division in California and a gold eagle for its author.

This boy, an American, came to high school from his home in Central Mexico and returned there on the completion of his course, entering the employ of an international mining corporation. He has pursued photography as a hobby and has won recognition in several national and international exhibitions. From the testing laboratory of the mining company he has advanced by successive steps to a responsible executive position.

CASE V—"THE CALIFORNIA CITRUS INDUSTRY"

This paper gave a complete description of the scientific aspects of the citrus industry dwelling particularly on the contribution of chemistry in fertilization, pest control, and the development of by-products. These latter have become a vital source of income dealing with fruit that is not up to standards of commerce. Formerly it went to waste. Chemistry has developed this industry, and definitely supervises its operation. In the preparation of this paper an extensive search of the literature was made, conferences were held with leaders in the industry and visits made to industrial plants dealing with citrus products. This paper was written in 1927-28, and took first place in its division in California and second place in the national contest. The paper was published in the California Citrograph and the National Chemistry Pamphlets.

The boy who wrote this paper entered the field of medicine, receiving the A.B. degree from Stanford University and the M.D. from Harvard. He made brilliant scholastic records in each institution. At present he is serving an internship in a Boston hospital. He has published the results of several research problems in the field of physiology.

These five case studies are those which stand out from many others. Among these have been problems which were concerned with testing a dairy herd for quality and quantity of milk, a study of the mineral content of irrigation water from various sources, a comparison of commercial brands of gasoline, the composition of the carbon deposit in the cylinder of an automobile engine, the deterioration of the cylinder oil in the crankcase of an automobile engine, and attempts at its regeneration. Through all the projects the development of the individual was the primary objective. In most cases the boys who made these studies have gone into some type of scientific or engineering work and have achieved beyond the level of the average high-school graduate.

If we subscribe to that philosophy of education which says that school is life, these pupils have been endowed at the high-school level with a superior quality and quantity of intelligence and have in this respect stood on a plane above their fellows. There can be little doubt but that their work on these extra-curricular projects gave to them a challenge to use their superior intelligence and in a measure trained them for superior achievement in adult life.

The discovery of such pupils and the possibility of their development is a privilege knocking at the door of every chemistry teacher in the land.

An IODOMETRIC METHOD *for the* ESTIMATION *of* SILVER

(For Student Use)

CLAUDE K. DEISCHER AND WALLACE M. McNABB

University of Pennsylvania, Philadelphia, Pennsylvania

THE authors wish to call attention to the fact that using ceric ammonium sulfate and starch as indicators, a standard solution of potassium iodide may be used in the titration of silver salts. The method has been verified by students in this laboratory and, therefore, can be recommended as a practical standard method for the estimation of silver in the presence of copper. The silver is titrated with standard potassium iodide in an acid solution forming insoluble silver iodide. After all the silver is completely precipitated, a permanent blue-green color is obtained.

The solubility of silver iodide, calculated from the solubility product (1.7×10^{-16}), is 3×10^{-6} grams per liter. This indicates that a suspension of silver

iodide in water in the presence of hydrogen ions gives a very low concentration of iodide ions. Since the oxidation potential of ceric to cerous ions is +1.55 volts, it is evident that this small concentration of iodide ions from silver iodide will not give a visible reduction of ceric ions. This is verified by adding to a suspension of silver iodide a few drops of a 0.1 *N* ceric ammonium sulfate and 3 cc. of starch solution. The absence of a blue-green color indicates that no reduction takes place. However, upon the addition of a drop of 0.1 *N* potassium iodide solution a blue-green color appears and is discharged immediately upon stirring, whereas the addition of a second drop gives a permanent blue-green color. Apparently the following reaction takes place.

$$2Ce^{++++} + 2I^- \rightleftharpoons 2Ce^{+++} + I_2$$

The second drop of potassium iodide solution increases the concentration of iodide ions to such an extent that the reaction is no longer reversible, and a permanent reduction is obtained, giving a blue-green color which remains, on stirring. This makes it possible for one to titrate a soluble silver salt with potassium iodide, knowing that the silver will precipitate as silver iodide before sufficient amount of iodide ions are present to reduce the ceric ions. The concentration of iodide ions necessary to reduce the ceric ions, after the silver is precipitated as silver iodide, is measured in the form of a blank and subtracted from each titration.

When silver is titrated in the presence of cupric ions and starch an indistinct endpoint is obtained; however, on the addition of ceric ions a satisfactory endpoint results. This might be expected from the difference between the oxidation potential of cupric to cuprous ion (+0.17 volt) and that of ceric to cerous ions (+1.55 volts). Since a larger excess of iodide ions are necessary to reduce a cupric than a ceric salt, it is possible to titrate silver in the presence of copper when ceric ions and starch are used as indicators.

A comparison was made of the gravimetric method (determination of silver as silver chloride) and Volhard method (titration of silver with ammonium thiocyanate) with the potassium iodide method. The analyses were made using pure silver nitrate in one case and an alloy containing 10 per cent copper. and 90 per cent. silver in another. Separate weighed samples were used for the silver nitrate, and aliquot portions of a solution containing the alloy were titrated for silver. Since the gravimetric and Volhard methods are well known, detailed directions are given only for the potassium iodide method.

The following procedure[1] was used for the titration of silver. Sufficient pure dry potassium iodide was weighed in order to give a 0.1 *N* solution. This was transferred to a liter measuring-flask and diluted to the mark. Five grams of the alloy were dissolved in nitric acid, the excess acid evaporated, transferred to a liter measuring flask, and diluted to the mark. Fifty cc. portions of the solution were transferred to a 250-cc. Erlenmeyer flask. To this were added water and a sufficient amount of sulfuric acid to give a volume of approximately 110 cc. (the concentration of acid may vary from 0.2 *N* to 3 *N*). Three cc. of 0.5 per cent. starch solution and 0.1 cc. of an approximately 0.1 *N* ceric ammonium sulfate solution were added. The silver was titrated with the standard potassium iodide solution. The endpoint was sharp and easily detected when the last drop of potassium iodide gave a permanent blue-green color to the solution. Blank titrations were made under the same conditions omitting the silver ion. The blank consumed 0.1 cc. of the potassium iodide solution before a permanent color was obtained.

TABLE 1

ANALYSIS OF ALLOY CONTAINING 10% COPPER AND 90% SILVER

	Volhard Method % Silver	*Potassium Iodide Method % Silver*	*Gravimetric Method % Silver*
	90.12	90.05	90.04
	90.04	90.00	90.01
Average	90.08	90.03	90.03
	ANALYSIS OF A SAMPLE OF SILVER NITRATE		
	63.38	63.37	63.42
	63.34	63.39	63.43
Average	63.36	63.38	63.41

SUMMARY

A method for titration of silver in the presence of copper is suggested for an experiment in quantitative analysis. For the first time, the method has been used by undergraduate students in this laboratory. For the first time, a comparison of this method with other standard methods has been made. The table gives results of analyses carried out by a sophomore in an undergraduate course of quantitative analysis.

[1] BLOOM AND MCNABB, *Ind. Eng. Chem., Anal. Ed.*, **8**, 167 (1936).

THE ELIZABETH CLAY HOWALD SCHOLARSHIP

This Scholarship, endowed by the late Ferdinand Howald, an alumnus of The Ohio State University, in memory of his mother, Elizabeth Clay Howald, carries a stipend of $3000 payable in twelve monthly installments.

Any person who has shown marked ability in some field of study and has in progress work, the results of which promise to constitute important additions to our knowledge, shall be deemed eligible to appoint to this Scholarship.

The Scholar will be expected to devote his time uninterruptedly to the pursuit of his investigations. If he has ever been a student of The Ohio State University or a member of the University staff, he may carry on his investigations either at The Ohio State University or, subject to the approval of the Graduate Council, elsewhere either in this country or abroad where superior advantages for his particular field of study are available. If the Scholar has never had any connection with The Ohio State University, however, then he must carry on his investigations at The Ohio State University.

Applications must be filed with the Dean of The Graduate School not later than March 1, 1938. The appointment will be made on April 1st and the term of appointment will begin July 1, 1938, and extend to July 1, 1939. Prospective candidates may secure application blanks by addressing The Dean of the Graduate School, The Ohio State University, Columbus, Ohio.

An EXPERIMENT *on* HETEROGENEOUS EQUILIBRIUM

ARTHUR A. VERNON

Rhode Island State College, Kingston, Rhode Island

AN ILLUSTRATION of the temperature-composition phase diagram of a two-component system is a valuable experiment in physical chemistry. The usual experiments involve a determination of the cooling curves of mixtures of metals and a plot of the diagram from the curves. When used in a large class, difficulty is often experienced with breakage of thermometers when the metal solidifies. Thermocouples are not practical for large numbers on account of the apparatus involved. In addition, cooling curves for other than the eutectic mixtures are frequently obtained which are not satisfactory for the determination of the temperature of initial separation of solid.

Briers[1] has suggested that *p*-toluidine and α-naphthol can be used for such an experiment. This system has two eutectic points and a point of compound formation. The solidification temperatures are all between 96° and 25°C. and the cooling curves can be obtained easily and quickly. It is the purpose of this article to describe the tests which have been made on this system and the experiment which has been developed. Ten mixtures are weighed as follows.

(1). 20 g. *p*-toluidine
(2). 17.6 g. *p*-toluidine plus 2.4 g. α-naphthol
(3). 15.1 g. *p*-toluidine plus 4.9 g. α-naphthol
(4). 11.0 g. *p*-toluidine plus 9.0 g. α-naphthol
(5). 8.5 g. *p*-toluidine plus 11.5 g. α-naphthol
(6). 7.6 g. *p*-toluidine plus 12.4 g. α-naphthol
(7). 6.6 g. *p*-toluidine plus 13.4 g. α-naphthol
(8). 4.0 g. *p*-toluidine plus 16 g. α-naphthol
(9). 2 g. *p*-toluidine plus 18 g. α-naphthol
(10). 20 g. α-naphthol

Each mixture is put into an eight-inch test-tube and a thermometer and glass stirrer fitted through a two-hole cork stopper. To determine a cooling curve, a tube is put into a beaker of water which need not be over 70°C. except for number nine and ten which require about 96°C. After the solid is melted and the liquid well stirred, the test-tube is supported in a beaker of water at 20°C. The temperature should immediately be noted and thereafter taken every fifteen seconds until all the material has solidified. While the cooling curve is being obtained, the mixture should be well stirred and the exact temperature at which solid first appears should be noted. For other than the eutectic and compound mixtures, this will be different from the temperature of final solidifications, and avoids the difficulty of trying to determine at what temperature the slope of the cooling line changes. From the temperature of initial separation of solid and of final constant temperature where the mixture becomes all solidified, the phase diagram can be plotted.

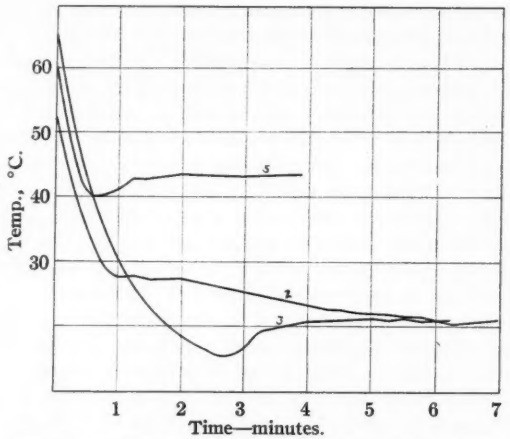


FIGURE 1.—COOLING CURVES OF *p*-TOLUIDINE-α-NAPHTHOL MIXTURES

Some typical cooling curves are given in Figure 1, and in Table 1 is listed the temperatures of initial solid separation and of solidification at the eutectic and compound points.

TABLE 1

CHARACTERISTICS OF *p*-TOLUIDINE-α-NAPHTHOL SYSTEM

Mixture	*Temperature of initial solid separation*	*Temperature of eutectic #1*	*Temperature of eutectic #2*	*Compound-Melting Point*
2	39°	32		
3	25.28—supercooled	31		
4	48			
5	51—supercooled			53.5
6	52.0		50.5	
7	49—supercooled		50	
8	65.5		49	
9	90			

These results are plotted in Figure 2 in which the points are labeled to show the mixture from which they were obtained. The temperatures were determined with a calibrated thermometer, and it is felt that the

[1] BRIERS, F., *Sch. Sci. Rev.*, **17**, 461 (1936).

accuracy is as good as is inherent in this method of determining a phase diagram. The results are easily reproducible except that sometimes a super-cooling is difficult to avoid. This introduces a possible error in the mixtures which are not the eutectic or compound compositions.

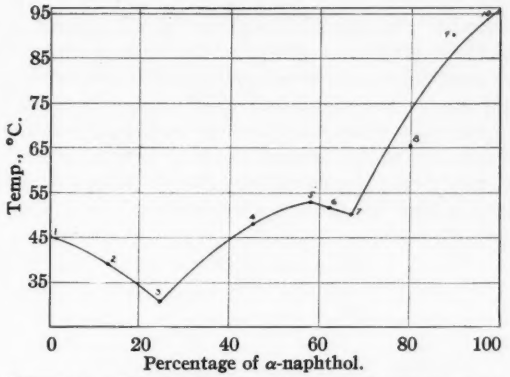


FIGURE 2.—TEMPERATURE-COMPOSITION DIAGRAM OF *p*-TOLUIDINE-α-NAPHTHOL SYSTEM

The experiment was given to a group of seniors majoring in chemistry and to a group of pre-medical senior students. The former group were more experienced in chemical technic, and thus a good comparison could be made between experienced and unexperienced students. It was found that both groups obtained temperatures which varied only a little more than the thermometer variations. A second trial usually gave more reliable data, and it is one of the advantages of this system that several cooling curves can be made in a short period of time.

On the basis of the results here presented, it is felt that the experiment described is satisfactory for use in a laboratory course in physical chemistry.

SUMMARY

1. An experiment illustrating a phase diagram of a two-component system is described.

2. Data is presented, and a phase diagram of the system *p*-toluidine-α-naphthol is shown.

A CYCLIC REACTION SCHEME ILLUSTRATING CARBOHYDRATE METABOLISM*

V. R. POTTER AND C. A. ELVEHJEM

University of Wisconsin, Madison, Wisconsin

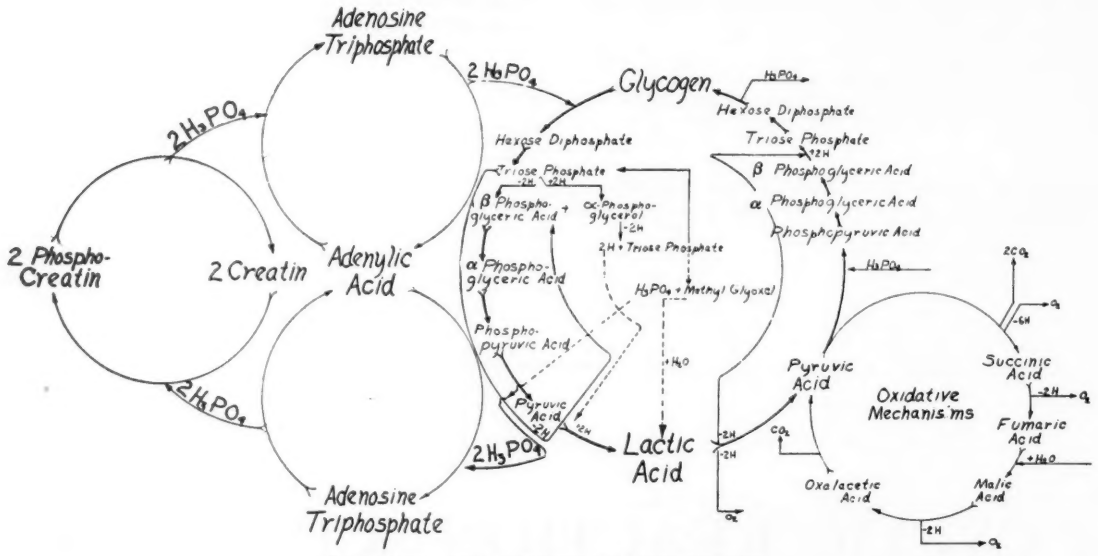
THE accompanying scheme illustrating carbohydrate metabolism was first worked out to illustrate graphically the reactions involved in muscle contraction. Later the oxidative reactions and the possible path of glycogen synthesis were added. It is believed that the resulting scheme represents an integrated concept of carbohydrate metabolism which is based on well-founded experimental data and which should be of interest to both students and teachers of biochemistry. This is particularly true because of the fact that the bulk of the confirmatory data is in journals not generally available. Also, the reactions are of greatest significance when seen in relation to the scheme as a whole. In this connection it seems worth while to mention that an important feature of the scheme is its *cyclic* nature. Portions of this scheme can be found in the literature in the form of reactions proceeding in *stages*. The use of a cyclic scheme emphasizes the *dynamic* aspect of the system.

Broadly speaking, the main reaction may be said to consist of the transfer of phosphate from phosphocreatine to glycogen by means of the intermediary breakdown and resynthesis of adenosine triphosphate. The hexose diphosphate thus formed breaks down to lactic

* Published with the permission of the Director of the Wisconsin Agricultural Experiment Station.

acid under anaërobic conditions. The phosphate liberated during this process is used for the resynthesis of phosphocreatine through the adenosine triphosphate system, and in the presence of air, the oxidative mechanisms furnish energy for the resynthesis of glycogen. It is readily seen that *phosphate transfer* is a dominant feature of the scheme, and that for all phosphorylations and de-phosphorylations we have the adenosine triphosphate-adenylic acid system acting as the phosphate donator and acceptor.

In 1925 muscle contraction was explained quite simply in terms of glycogen breakdown to lactic acid. However, in 1927 the Eggletons (*1*) reported the finding of of phosphopyruvic acid while creatine is not needed for this reaction. Adenosine triphosphate is needed for the phosphorylation of creatine and phosphopyruvic acid is not needed here. This point is illustrated quite clearly in the chart. Very recently Lehmann and Needham (*10*) have published a paper showing the nature of the reactions in which creatine and glycogen compete for the phosphate which comes from phosphopyruvic acid via adenylic acid, and have found that pH is probably the governing factor. Some inorganic phosphate may be esterified without passing through adenylic acid, but the importance of this reaction is still questionable.



CATABOLISM AND ANABOLISM OF CARBOHYDRATES

"phosphagen" in muscle, and this was shown to be phospho-creatine by Fiske and Subbarow (*2*). Lohmann (*3*) isolated adenosine triphosphate from muscle in 1929 and two years later Meyerhof and Lohmann (*4*) suggested that the rôle of the compound as coenzyme in muscle glycolysis consists in the initial esterification of carbohydrate by the labile phosphoric acid groups, the triphosphate being resynthesized at a later stage in the carbohydrate breakdown. In 1934 Lohmann (*5*) showed that the splitting of phosphocreatine in dialyzed muscle extracts takes place *only in the presence of adenylic acid*, which is simultaneously converted into adenosine triphosphate. The reverse Lohmann reaction, *i. e.*, the resynthesis of phosphocreatine from creatine and adenosine triphosphate, has been demonstrated by Meyerhof and Lohmann (*6*), Lehmann (*7*), and by Needham and van Heyningen (*8*). The above papers, together with a report by Ostern *et al.* (*9*), indicated that phosphopyruvic acid served as the source of phosphate in the reverse Lohmann reaction. Adenylic acid appears to be necessary for the dephosphorylation

In 1933 Embden, Deuticke, and Kraft (*11*) proposed a scheme of glycogen breakdown in which hexose diphosphate formed β-phosphoglyceric acid and α-phosphoglycerol as shown in the figure. According to Embden, the phosphoglyceric acid formed pyruvic acid, which was then reduced to lactic acid by α-phosphoglycerol, which was thus oxidized back to triosephosphate (phosphoglyceraldehyde and phosphodihydroxy acetone). This reduction of pyruvic acid has been well supported by experimental data, but it is shown in dotted lines on the chart because it is perhaps quantitatively less important than the reduction of pyruvic acid by triosephosphate as shown by Meyerhof and Kiessling (*12, 13*). In the latter reaction

phosphoglyceraldehyde + pyruvic acid → phosphoglyceric acid + lactic acid

The phosphoglyceric acid then rearranges to yield more pyruvic acid and thus the main path of glycogen breakdown probably proceeds as indicated. The Embden-

Meyerhof scheme does not include methylglyoxal, but it would seem that this substance may still have a significant rôle in lactic acid formation even though it has been shown that lactic acid can be formed by another mechanism. There are indications that not all tissues form lactic acid via phosphorylated intermediates, and that in those which utilize glucose without phosphates methylglyoxal is involved (see Geiger (*14*)).

In the presence of oxygen, lactic acid is oxidized to pyruvic acid. It has been known for many years that lactic acid could be converted to glycogen under aërobic conditions in which a part of the lactic acid was oxidized to furnish energy for the synthetic reaction. Elliott and Schroeder (*15*), and Elliott, Benoy, and Baker (*16*) have proposed a series of reactions which can be presented as shown in the chart under "oxidation mechanisms." A similar series of reactions was previously described by Hahn (*17*) for muscle tissue. It should be noted that in the oxidative cycle, *two* molecules of pyruvic acid begin the reaction and *one* is formed again at the completion of the cycle. The quantitative relations and the extent to which the reversible systems function as hydrogen carriers is still unsettled. Szent-Györgyi *et al.* (*18*) consider the fumarate system to be an important hydrogen carrier, and there is evidence to show that only a small part of the oxalacetate is decarboxylated (*19*). The possibility that oxalacetate and lactate react to form pyruvate and malate should also be mentioned (*19*). The chart shows only the main paths of breakdown.

As far as the authors are aware, no one has postulated the scheme for glycogen synthesis which is shown in the chart. The evidence in favor of it is worth considering, however. Von Euler and Günther (*20*) obtained carbohydrate synthesis *in vitro* from both lactic and pyruvic acids, using liver slices from fasted rats. The *in vivo* reaction has, of course, been known for many years. Meyerhof and Kiessling (*21*) have shown that α-phosphoglyceric acid, β-phosphoglyceric acid, and phosphoenol-pyruvic acid exist as an equilibrium mixture in muscle extract, and the conversions are completely reversible. Thus phosphopyruvic acid would be converted to β-phosphoglyceric acid if the latter were removed as fast as it was formed. The phosphorylation of pyruvic acid has not as yet been demonstrated. The course of the reaction may well be determined by the oxygen tension and pH.

The authors do not believe that a reaction scheme of this type must represent the ultimate truth regarding the mechanisms involved in order to justify its existence. As soon as new data are found the scheme can be modified accordingly. Meanwhile, the scheme gives a concise and integrated picture of the probable reaction paths. It should be mentioned that all of the compounds shown have been isolated, and in many cases synthesized and substituted into the postulated reaction.

LITERATURE CITED

(1) EGGLETON, P. AND G. P. EGGLETON, "The inorganic phosphate and a labile form of organic phosphate in the gastrocnemius of the frog," *Biochem. J.*, **21,** 190–6 (1927).

(2) FISKE, C. H. AND Y. SUBBAROW, "Phosphocreatine," *J. Biol. Chem.*, **81,** 629–81 (Mar., 1929).

(3) LOHMANN, K., "Über die Pyrophosphatfraktion in Muskel," *Naturwissenschaften*, **17,** 624–5 (1929).

(4) MEYERHOF, O. AND K. LOHMANN, "Über die Energetik der anaeroben Phosphagensynthese ("Kreatinphosphorsäure") im Muskelextrakt," *ibid.*, **19,** 575–6 (1931).

(5) LOHMANN, K., "Über die enzymatische Aufspaltung der Kreatinphosphorsäure; zugleich ein Beitrag zum chemismus der Muskelkontraktion," *Biochem. Z.*, **271,** 264–78 (1934).

(6) MEYERHOF, O. AND K. LOHMANN, "Über energetische Wechselbeziehungen zwischen dem Umsatz der Phosphorsäureester im Muskelextrakt," *ibid.*, **253,** 431–62 (1932).

(7) LEHMANN, H., "Über die enzymatische Synthese der Kreatinphosphorsäure durch Umesterung der Phosphobrenztraubensäure," *ibid.*, **281,** 271–92 (1935).

(8) NEEDHAM, D. M. AND W. E. VAN HEYNINGEN, "The linkage of chemical changes in muscle extract." *Biochem. J.*, **29,** 2040–51 (Sept., 1935).

(9) OSTERN, P., T. BARANOWSKY, AND J. REIS, "Über die Verkettung der chemischen Vorgänge im Muskel. VIII. Phosphoglycerinsäure und Adenylsäure," *Biochem. Z.*, **279,** 85–94 (1935).

(10) LEHMANN, H. AND D. M. NEEDHAM, "Competition between phosphorylating enzymes in muscle extract," *Biochem. J.*, **31,** 329–39 (Feb., 1937).

(11) EMBDEN, G., H. J. DEUTICKE, AND G. KRAFT, "Über die intermediären Vorgänge bei der Glycolyse in der Muskulature," *Klin. Wochschr.*, **12,** 213–5 (1933).

(12) MEYERHOF, O. AND W. KIESSLING, "Die Umesterungsreaktion der Phosphobrenztraubensäure bei der alkoholischen Zuckergärung," *Biochem. Z.*, **281,** 249–71 (1935).

(13) MEYERHOF, O. AND W. KIESSLING, "Über den Hauptweg der Milchsaürebildung in der Muskulatur," *ibid.*, **283,** 83–113 (1935).

(14) GEIGER, A., "Role of glutathione in anaërobic tissue glycolysis," *Biochem. J.*, **29,** 811–24 (Apr., 1935).

(15) ELLIOTT, K. A. C. AND E. F. SCHROEDER, "The metabolism of lactic and pyruvic acids in normal and tumour tissue I. Methods and results with kidney cortex," *ibid.*, **28,** 1920–40 (1934).

(16) ELLIOTT, K. A. C., M. P. BENOY, AND Z. BAKER, "The metabolism of lactic and pyruvic acids in normal and tumour tissues. II. Rat kidney and transplantable tumours," *ibid.*, **29,** 1937–51 (Aug., 1935).

(17) HAHN, A., "Über Dehydrierungsvorgänge im Muskel," *Z. Biol.*, **92,** 355–66 (1932).

(18) ANNAU, E., I. BANGA, B. GÖZSY, ST. HUSZAK, K. LAKI, B. STRAUB, AND A. SZENT-GYÖRGI, "Über die Bedeutung der Fumarsäure für die tierische Gewebsatmung," *Z. physiol. Chem.*, **236,** 1–68 (1935).

(19) ANNAU, E., I. BANGA, S. BLAZSO, V. BRUCKNER, K. LAKI, F. B. STRAUB, AND SZENT-GYÖRGI, A., "Über die Bedeutung der Fumarsäure für die tierische Gewebsatmung," *ibid.*, **244,** 105–52 (1936).

(20) VON EULER, H. AND G. GUNTHER, "Zur Kenntnis der Kohlenhydrat-Resynthesis in der Leber," *ibid.*, **243,** 1–9 (1936).

(21) MEYERHOF, O. AND W. KIESSLING, "Über den enzymatischen Umsatz der synthetischen Phosphobrenztraubensäure (enolbrenztraubensäure - phosphorsäure)," *Biochem. Z.*, **280,** 99–110 (1935).

SOME PRACTICAL HELPS *in* ORGANIC ANALYSIS

G. H. CHEESMAN

Norwood Technical Institute, London County Council, London, England

THE following notes may prove useful in technical analysis and also for those teaching organic analysis. They have been incorporated into the standard scheme taught to organic chemistry students here and do not appear to have been described before.

A TEST FOR PRESENCE OF ESTERS

In examining organic materials for the presence of saponifiable matter it seems desirable to have a simple, rapid, and specific test which consumes little material. The ordinary method of boiling with alkali and examining the products to ascertain whether hydrolysis has occurred is wasteful of time and material if no ester be found.

If almost any of the esters commonly met with in technical solvents, or offered to students for analysis, be refluxed with alcoholic alkali hydroxide, saponification proceeds rapidly and completely. By using a quantity of alkali less than sufficient to complete the saponification, the occurrence of the reaction may be detected by observing the disappearance of the alkalinity.

The amount of alkali required for this purpose may be arrived at by considering the highest ester likely to be encountered: thus, benzyl benzoate (mol. wt. 212) will require 2.3 cc. of 2 *N* alkali per gram for its complete saponification. Assuming the density of esters to be about 1, we may say that most esters will react with more than twice their own volume of 2 *N* alkali, and hence we may apply this as a test as follows.

To a portion of the liquid to be tested, neutralized if necessary by addition of acid or alkali, add a quarter of its volume of 2 *N* caustic potash in methanol (this solution keeps indefinitely), reflux for five minutes, and dilute with its own volume of cold water. The presence of esters is indicated by the solution then remaining colorless on the addition of phenolphthalein.

It is convenient to perform this test in an ordinary boiling tube with a very simple reflux condenser.

SAPONIFICATION OF ESTERS IN THE PRESENCE OF HYDROCARBONS, ETC.

When water-insoluble esters are being saponified with aqueous alkali (with the object of recovering the products for recognition), and particularly if hydrocarbons or similar substances be present, the amount of organic material in the aqueous phase is so small that the saponification proceeds at a very slow rate. On the other hand, the use of alcoholic alkali complicates the identification of the ester-alcohol. In such a case, the use of alkali dissolved in a mixture of pyridine and water greatly accelerates the process, and the pyridine can readily be removed at a later stage. Thus, as an example, the liquid may be refluxed for two hours with five times its volume of 2 *N* aqueous potassium hydroxide and the same volume of pyridine. The non-acidic products of saponification and the pyridine are then removed by distilling down to small bulk, and separated from one another by redistillation after addition of sulfuric acid. This second distillate will contain the alcohol from the ester, together with the hydrocarbons, etc., originally mixed with it, and but little pyridine. The acid from the ester will remain in the residue from the first (alkaline) distillation.

The action of the pyridine seems partly to be due to its promoting mixing of the layers, but experiments with other materials which dissolve readily in both layers seem to indicate that it does actually take part in the saponification process to some extent.

SEPARATION OF ALCOHOLS FROM MIXTURES WITH ESTERS, HYDROCARBONS, ETC.

Liquid mixtures boiling below about 170° may conveniently be separated by conversion of the alcohols to their benzoic esters which boil considerably higher. A convenient procedure is as follows. Dry the liquid for one hour over anhydrous sodium sulfate, filter and add an equal volume of pure dry pyridine, followed by a slight excess of benzoyl chloride added slowly in small portions with vigorous shaking, keeping the temperature below 20°; should the mass become solid during the addition, dilute with more pyridine. When the addition is complete (the cessation of heat evolution is a good indication of this), allow the mass to stand a while. Wash well with plenty of water, then with dilute hydrochloric acid, and finally with water. (These washings will contain any water-soluble substances, other than alcohols, present in the original material.) Dry and transfer to a distilling flask. Place in an oil bath and raise the temperature of the bath slowly to 200°. Collect the distillate till no more passes over at this temperature. The distillate contains the hydrocarbons, etc., from the original material, while the benzoates of the alcohols remain in the residue, which may be saponified to recover them, or fractionated to identify them by their boiling points. In addition to the benzoates, the following compounds may be

present: benzaldehyde (b. p. 179°); benzoyl chloride (b. p. 198°); benzoic acid (b. p. 250°—tends to solidify in the condenser) and benzoic anhydride (b. p. 360°).

A NEW AND INEXPENSIVE SODIUM PRESS*

E. H. PARKE

Oberlin College, Oberlin, Ohio

A BLOCK of steel (*A*), 5 inches long and 1 inch square, is drilled its entire length with a $^{5}/_{8}$-inch drill. A slot (*D*) is then cut through the middle part of this block, 2 inches long and $^{5}/_{8}$ inch wide. Next one end of the drilled opening (*a*) is threaded with an 18 thread.

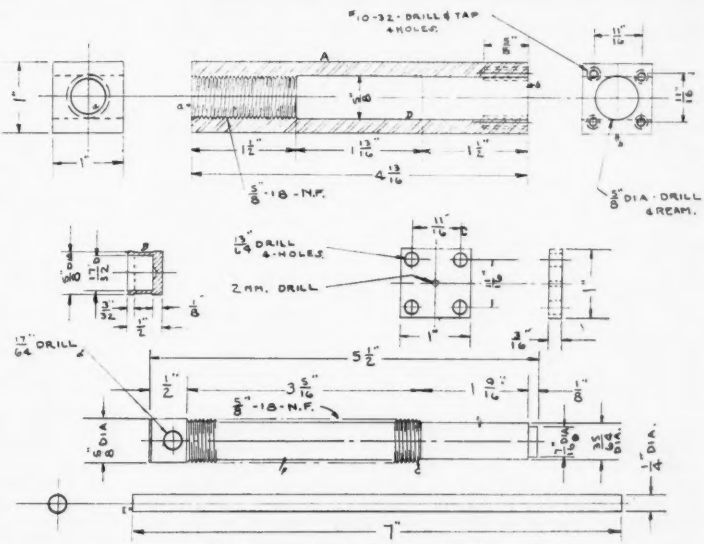
On the lathe a piece of hard brass (*B*), $^{1}/_{2}$ inch long, is now turned out to fit closely in the lower end of the block (*b*). In one end of this brass block a $^{1}/_{2}$-inch hole $^{1}/_{4}$ inch deep is drilled.

A piece of steel rod (*F*) $5^{1}/_{2}$ inches long is turned to such a diameter that, when threaded, it can be screwed into the threaded part of the steel block (*A*) already described. This rod, or plunger (*F*) as it will be, should be threaded a distance of $3^{1}/_{4}$ inches from a point $^{3}/_{4}$ inch from the end. In this unthreaded space there is drilled a hole (*a*), $^{1}/_{4}$ inch, for the lever handle (*E*) mentioned later. From the inner end of the threading (*c*) the rod should be turned $^{1}/_{32}$ inch smaller, and for just $^{1}/_{4}$ inch at the extreme end $^{1}/_{32}$ more. This tip when in use will work in the opening in the brass block (*B*) mentioned above and will push, rather than turn, this block against the sodium.

A square plate of hard steel (*C*) is now fitted to the lower end of the cylinder block with four $^{13}/_{64}$-inch stud screws, one in each corner. In the center of the plate a hole of convenient size (1.5 to 2 mm.) is drilled for the extruding of the sodium in wire form. The lever handle (*E*) is of $^{3}/_{16}$-inch hard steel.

The press is now ready for filling, which is done by putting small pellets of sodium into the cylinder through the slot (*D*) or through the lower end with the plate (*C*) off. The former is preferable. After putting in as much sodium as possible, the brass block (*B*) is placed directly behind it and forced in with the plunger. Considerable pressure will be needed before any of the metal will be extruded, but nearly all can be pressed out by this procedure. When the press is emptied, the plate should be removed, the brass block pushed out, and the operation repeated.

This cylinder will be found to be quite air-tight and the sodium contents kept quite free from oxidation except, perhaps, for the tiny part remaining in the hole in the plate. This little section should be snipped off upon extrusion.



AN INEXPENSIVE SODIUM PRESS

The filling should be done quickly, so that the metal will take on as little air moisture as possible.

Any small vise will hold the press to the table, but Cenco's table vise No. F191 has been found satisfactory. The screw on the long side should be cut off.

This press can be made by anyone familiar with a lathe.

* See Editor's Outlook.

William O. Brooks
A. T. Burtsell
R. K. Carleton
Tenney L. Davis
C. K. Deischer
J. Howard Graham
B. Clifford Hendricks

ABSTRACTS

J. W. Howard
D. C. Lichtenwalner
Greta Oppe

C. M. Pruitt
Leopold Scheflan
A. A. Vernon
E. D. Walter
Mary Elvira Weeks
Sidney Weinhouse
G. H. Woollett

KEEPING UP WITH CHEMISTRY

Colloidal silica. A. King. *Sch. Sci. Rev.*, **19**, 16–22 (Oct., 1937).—Theoretically, it should be possible to obtain any substance in the form of a colloid, and in practice most of the elements and their simple compounds have been so prepared. The colloidal state is thus to be regarded as a physical state similar to the solid, liquid, gaseous, and dissolved states in which all kinds of matter may exist. Colloidal silica may be obtained in the pure state by hydrolysis of the sulfide, chloride, or the fluoride of silicon, but is generally prepared by the addition of an acid to water glass. The product is generally described as the sol of silicic acid, but it is more probable that the sol is essentially a colloidal suspension of silica.

According to the method of preparation and consequent aggregation of the primary particles, the specific surface of silica may vary within wide limits, and with it, as may be expected, the chemical and physical properties in general. Although gelatinous silica resembles gelatin, agar, and other gels in many respects, there are some very fundamental differences between the two types, the most obvious of which is the irreversibility of silica gel. Since electrolytes readily diffuse into silica gel, it is possible to make chemical reactions take place by slow double decomposition in this medium, undisturbed by convection, etc. The products of such reactions take the form of large, regular crystals, in contrast to the small or amorphous aggregates formed by direct mixing of the solutions. In this manner, magnificent crystals of gold, silver, etc., may be prepared; and this mechanism of formation has been used to explain the formation of gold crystals in quartz, which at one time existed as a hydrated silica gel.

Commercial adsorbent silica is usually prepared by precipitating a gel by the action of HCl upon water glass and then washing free of sodium chloride with hot water. Various methods have been attempted to improve the adsorptive capacity of the gel, one of the most interesting of which is due to Holmes and co-workers [*Ind. Eng. Chem.*, **17**, 280 (1925)], who added ferric chloride to water glass until neutral, dried the precipitate, and dissolved out the ferric hydroxide with hydrochloric acid, leaving a colorless, highly porous gel. This process was even more successful when copper sulfate was substituted for ferric chloride. As a technical drying agent, partially dehydrated silica gel finds great use in the drying of air for blast furnaces, in the purification and drying of gases, and for general domestic and cosmetic purposes. It is also used for the removal of sulfur compounds from oils, and as a filtering agent, to purify and decolorize vegetable oils, pharmaceutical preparations, etc. In spite of its highly porous nature, adsorbent silica is not a very good catalyst, yet perhaps its most important technical application is as a carrier for platinum and other catalysts used in the contact process of sulfuric acid manufacture. S. W.

Mixed melting points. H. C. Palmer. *Sch. Sci. Rev.*, **19**, 131 (Oct., 1937).—A sheet of copper about eight inches by one inch is balanced on a flat plane, such as the stopper of a bottle. At one end at right angles to the axis of the strip three small piles are formed of the substances, A, B, and a mixture of A and B. An inch or so in front of these piles place a "sentry" pile of one of the substances. Now heat the other end of the strip and watch the sentry. As soon as it has melted transfer attention to the three piles. If A and B are identical all three will melt together; if not, the middle one will melt long before the others. S. W.

Solubility product. A. J. Mee. *Sch. Sci. Rev.*, **19**, 131 (Oct., 1937).—The solubility product of lead iodide may be shown to be constant at room temperature by adding small quantities of M/10 lead acetate and M/10 potassium iodide to 50 cc. of water. Fixed quantities of one solution are added to the water, and the other solution run in out of a buret until a silky yellow precipitate is formed. The concentrations of the ions may then be calculated assuming complete dissociation, and the product $(Pb)(I)^2$ is constant. A more definite precipitation point may be obtained by using M/5 solutions, but the results do not seem to be quite so concordant. S. W.

Water pollution and health. M. Trumper. *Chemist*, **14**, 261–4 (Nov., 1937).—Water is so fundamental to our existence that we accept it as a matter of course. Our interest in it becomes aroused when the supply fails or becomes markedly contaminated.

Wherever water supplies are taken from upland reservoirs, because of the very few sources of contamination, we get a drinkable draft. In cities where streams and rivers polluted with industrial trade wastes are used as sources of drinking water, the recipe for our water cocktail is something like this: plenty of alum or aluminum sulfate, some soda-ash and lime, and always plenty of chlorine, with a dash of copper sulfate and permanganate.

In former years the typhoid-producing germ ranked as public enemy number one. In this, public health and water works officials have waged a successful war. Their chemical barrage has kept the typhoid enemy in no man's land.

What has our community done and what is it doing to secure good water? The general public has reason to be grateful to sportsmen for their activity in behalf of pure streams. Today we have the men with the chemical knowledge to insure potable water. The sportsmen and the toxicologist unite in striving to keep the streams safe for fish. If we keep our streams safe for fish, we shall keep them reasonably safe for human beings. Fish are excellent indicators of the presence of poisonous chemicals in the water. They are very sensitive to ammonia, but different fish show varying degrees of sensitivity to copper sulfate. Fish will die if there is too little oxygen in the water, which always indicates pollution. Fish will die when some strong chemical kills off the small forms of aquatic life which in turn clog up the gills of the fish.

The perennial question of water pollution abatement is now being recognized as demanding action. The technical knowledge available today would insure a substantial reduction of the pollution load on our waters. Industry invariably protests because of the excessive costs. Likewise, when a pure stream bill comes before the state legislature creating power to act against the pollution of our streams, one hears much about the constitutionality of the pending legislation. R. K. C.

A filter pump aid. J. H. Feiner. *Chemist-Analyst*, **26**, 4, 92 (Oct., 1937).—In using a filter pump and suction flask, water is often sucked back into the filtrate, even when stop devices are used. If in making the trap, a Bunsen valve is used on the tube leading to the suction flask, this trouble is eliminated. Water may enter the bottle, but the Bunsen valve closes, stopping the water. In addition, suction can be maintained in the suction flask after the water pump has been disconnected, so that for slow filtering substances, filtration may be continued overnight. D. C. L.

Synthetic aliphatic penetrants. B. G. Wilkins and J. N. Wickert. *Ind. Eng. Chem.*, **29**, 11, 12, 34–9 (Nov., 1937).—Much interest has been displayed in organic compounds which possess properties of surface activity in water solutions. Many patents have been issued for the manufacture of compounds to be used as wetting agents, penetrants, detergents, emulsifying, and spreading agents. These substances are of interest to the textile, leather, insecticide, paper ceramics, pharmaceuticals, metals, paints, cosmetic, and other industries. Soaps and similar

types of compounds consist of a hydrocarbon portion of high molecular weight at some point in which is located a water-soluble group to enable at least colloidal dispersion in water. To reduce sensitivity to hard water, carboxyl groups have been changed to alcohols and water solubility increased by sulfonation. In this article a group of Na secondary alcohol sulfates in which the hydroxyl groups are near the center of the molecule, group B, are compared with the type in which the water-soluble groups are at the end of the chain, group A. Group A appears to be superior in regard to detergent and emulsifying properties; group B is superior in penetrating power and wetting action. Graphs showing penetration, wetting action, surface tensions, and lime soap dispersibility with varying pH are given. These are of importance in wool carbonizing, acid fruit washing, cotton kier boiling, and dyeing operations. D. C. L.

The increase of bodily activities by artificial changes of the acid-base condition (in man). H. DENNIG. *Chem.-Ztg.*, **61,** 526–7 (June 26, 1937).—It was found that by the intake of acids, causing a state of acidosis, a man becomes exhausted very quickly upon carrying out some strenuous bodily activities. On the other hand, when a state of alkylosis is produced the efficiency is greatly increased. Such alkylosis was produced by the intake of potassium or sodium carbonate as well as sodium citrate in harmless amounts and became noticeable after two days. The same effect can be produced by the elimination of meat, bread, and the usual flour products from the diet and substituting in their place milk, certain vegetables, and a large amount of soy flour. L. S.

The rapid determination of manganese in aluminum and aluminum alloys. K. ALTMANNSBERGER. *Chem.-Ztg.*, **61,** 618 (July 24, 1937).—Dissolve 0.2 gram of sample in 20 cc. 1:1 H_2SO_4 in an 800-cc. Erlenmeyer flask and dilute to 300 cc. Add 10 cc. of silver nitrate solution (5 g./l. of water) and 30 cc. ammonium persulfate solution (60 g./l. of water). Boil until the evolution of gas has stopped, cool quickly in cold running water, and titrate the cold, wine-red solution with arsenic acid solution (0.4 g. As_2O_3/l. of water) which had been standardized against a known sample (*e. g.*, steel containing 0.28 per cent. carbon and 1.12 per cent. manganese). This method is particularly adapted for manganese contents from 0.1 to 2 per cent.

$$2MnSO_4 + 5(NH_4)_2S_2O_8 8H_2O = 2HMnO_4 + 5(NH_4)_2SO_4 + 7H_2SO_4$$

$$MnO_2 + H_3AsO_3 + H_2SO_4 = MnSO_4 + H_3AsO_4 + H_2O$$

The titration can be repeated after renewed oxidation with persulfate. A numerical example is given. L. S.

Helium. K. PIETRUSKY. *Chem.-Ztg.*, **61,** 661–2 (Aug. 14, 1937).—A discussion of chemical and physical properties, the American helium industry, cost of production, and legal status. L. S.

Gas analysis in the Orsat apparatus. GEHLE. *Angew. Chem.*, **50,** 693–5 (Aug. 14, 1937).—The following conclusions are drawn from experimental studies. By means of activated palladium it is possible to burn methane with oxygen at low temperatures with a low temperature limit of about 400°C. The activation occurs by the catalytic combustion of hydrogen during prolonged red glow of the wire. No fractional hydrogen combustion is possible over activated palladium. The use of palladium tubes in addition to the copper oxide tube makes it possible to eliminate the use of high temperatures with their undesirable influences and renders possible the reliable determination of ethane from the consumption of oxygen. The preparation of pure oxygen by means of chemicals is simpler than its removal from a cylinder. An accurate combustion analysis can be carried out by burning a sample in a combustion tube and attachment of this tube by means of a capillary bridge to the two ends of the Orsat apparatus. L. S.

Cuprene as a cork substitute. F. FRITZ. *Chem.-Ztg.*, **61,** 737 (Sept. 11, 1937).—Various methods of manufacturing cuprene (chemical composition $(C_7H_6)_n$) are described. It can be obtained in the form of a brown mass which can be cut and may be used as a substitute for cork. L. S.

Sugar from wood. R. SCHARF. *Z. phys. chem. Unterricht.*, **50,** 202–4 (Sept.-Oct., 1937).—Two commercial processes are available for the manufacture of sugar from wood, the Bergius and the Scholler processes. Both methods involve the treatment of wood with acids whereby cellulose is hydrolyzed to simple sugars which dissolve while lignine remains undissolved. Bergius uses highly dried wood and forty per cent. hydrochloric acid at 20°C. at atmospheric pressure, filters the sugar solution, evaporates *in vacuo* to recover the hydrochloric acid and dries the product obtained. The dried sugar still contains one per cent. hydrochloric acid which is neutralized. Scholler uses 0.4 per cent. sulfuric acid at 170°C. at a pressure of eight atmospheres and does not require the use of dried wood. After filtration the excess acid is neutralized. One ton of pine wood will yield 400–600 kilograms of fermentable sugar. The mixture of sugar obtained has this composition: sixty-two per cent. glucose, twenty-five per cent. mannose, four per cent. galactose, one per cent. fruitose, and eight per cent. xylose. The Bergius method may be demonstrated as follows for teaching purposes. About two grams of wood flour are placed together with 25 cc. of concentrated hydrochloric acid of a specific gravity of 1.19 in a flask which is then tightly closed and well shaken. The color changes from yellowish green to dark green while the first stiff mass becomes thin fluid. Half an hour later the mixture is treated with 25 cc. of water and filtered. The filtrate is rendered slightly alkaline with sodium hydroxide and the presence of sugar is proven by means of Fehling's solution. L. S.

Alcohols from sugar by electrolytic reduction. D. H. KILLEFFER. *Ind. Eng. Chem., News Ed.*, **15,** 489–90 (1937).—Very pure dextrose is dissolved in distilled water with the addition of salts to accomplish enolization and give conductivity. The solution is introduced into electrolytic cells, where reduction to hexahydric alcohols takes place in the cathode compartment. It is handled throughout in rubber or glass-lined equipment. The solution from the electrolytic cells is conducted to glass-lined vacuum evaporators where the water content is reduced. The solid residue from evaporation is treated with hot ethyl alcohol to dissolve the hexahydric alcohols from the insoluble salt. The mixture is filtered in glass-lined filters and the alcohol solution cooled to crystallize out the mannitol. The crude mannitol is recrystallized from water. The alcoholic mother liquor from the mannitol crystallization is decolorized with carbon and evaporated to recover the sorbitol. Due to the tenacity of sorbitol for water it is marketed as an eighty-five per cent. sirup. Mannitol may be nitrated to an explosive, while sorbitol is valuable as a softening agent and as an intermediate for the production of ascorbic acid. A. A. V.

Sorbitol from glucose by electrolytic reduction. R. L. TAYLOR. *Chem. & Met. Eng.*, **44,** 588–91 (Oct., 1937).—Until very recently sorbitol was known to chemical engineers as little more than a rare curiosity, selling for from three hundred dollars to five hundred dollars a pound. Likewise, mannitol was known as the chief constituent of manna and used only in the medicinal field.

During the recent depression the Atlas Powder Company developed a process for making sorbitol and mannitol by the electro reduction of dextro glucose. An anode of pure lead and a cathode of lead-mercury amalgam is used. Completely surrounding each anode is a diaphragm of unglazed porcelain which encloses the dilute sulfuric acid anolyte and keeps it apart from the glucose solution which serves as the catholyte. The water in the two electrolytic solutions is decomposed by the current to liberate at the cathode nascent hydrogen which reduces the glucose to sorbitol and mannitol and at the anode nascent oxygen which forms lead peroxide. As the electrolyte heats up during the process it is run through a cooling coil and recycled through the cell. The solution is finally removed and evaporated, leaving mannitol, sorbitol, and sodium sulfate. These two alcohols are removed from the sulfate by hot ethyl alcohol. The alcohol solution is then chilled until the mannitol crystallizes out. These crystals are separated from the sorbitol solution by means of a centrifuge. The sorbitol solution is further concentrated to approximately an eighty-five per cent. water solution.

In general characteristics these compounds differ only in degree from those of ethylene glycol and glycerine.

Sorbitol can be used as a conditioning agent for textiles, paper, leather, and also as a starting material for making many organic compounds.

Mannitol is used in medicinal fields and for making fancy papers and resins. Nitro-mannite is useful in medicine and as a non-corroding primer for explosives. J. W. H.

The versatile stearates. J. A. SINGMASTER, JR. *Chem. Industries*, **41,** 234–7 (Sept., 1937).—When a new chemical product suddenly rockets into sight, an accurate record is seldom kept of just what started it on its course, who had the inspiration, and whether it was chance or careful planning. So it was with the stearate industry. Many stories are told of how these chemicals practically lifted themselves by their own boot-straps to the position of importance they now occupy.

One such story, which has its setting more than fifteen years ago in the Mallinckrodt plant, runs as follows. A salesman learned that the company had been doing research with a chemical known as aluminum stearate, which had unique properties but was used only in small quantities for a few special purposes. At that time twenty or thirty barrels of aluminum stearate was considered a large stock.

The salesman was told that among other things aluminum

stearate would cause oils to jell. Knowing of a company which did a large business in lubricants, he dropped in one day and found they were having trouble disposing of a certain oil. He offered a sample of a chemical which, he predicted, could be added to the oil and heated to produce a grease of very interesting properties.

The sample was sent, and nothing more was heard for some time. Then the oil company one day ordered a ton of aluminum stearate. They had made a fine grease of beautiful appearance and immediately found a small market for it. Again there was a long silence, when to the complete consternation of the production department, there came an order for a carload. A carload of aluminum stearate had never been shipped before, and the quantity the railroad stipulated as a minimum carload could not be loaded into the largest freight car available.

Up to that time a carload of aluminum stearate would have represented a high percentage of the total annual production. Now it would be only a fraction of one per cent., for during the past decade the stearates have found many new uses in a wide variety of industries.

This is due to the general chemical progress coupled with the increasing knowledge that these substances have unique chemical and physical properties of value. Chemists and production engineers have learned that they facilitate many otherwise difficult production processes and are valuable ingredients for many products. And it is not alone in new industries and for new products that they are being increasingly used; many older products have been improved by them.

Stearates are valuable to many industries because of certain unusual physical and chemical properties not found to quite the same degree in other materials. Physically the stearates are smooth, slippery powders. When rubbed between the fingers they form a slick, smooth coating on the skin. Because of this property zinc stearate is a well-known dusting powder, widely used in the cosmetic industry. This same property makes the stearates useful in the dry state as lubricants for molding and extruding operations, wire drawing, metal stamping, cartridge making, etc., as release agents in the plastic industry, and as anti-sticking agents in the rubber industry.

Because metallic stearates are insoluble in water, they are especially useful in certain types of waterproofing. When small quantities are mixed in the dry form with cement, the pores of the finished concrete become lined with a thin film of the water-repellent stearate which destroys their capillary action and so prevents absorption and transmission of water. For the same reason they are often added to the mortar used for laying bricks. Moisture is prevented from seeping up through the joints and eventually penetrating the bricks to produce an unsightly efflorescence on the exterior.

Calcium and aluminum stearates, incorporated in suitable solvents, make waterproofing liquids that will impregnate many materials, such as textiles, leather, ropes, ceramics, etc.

Other large-scale industrial applications of the stearates include their use in crayons and their use as anti-oxidants in transformer oils. All told, more than a dozen different industries now use the stearates in large quantities in the manufacture of numerous products. They have demonstrated a usefulness and value to industry far beyond even the wildest dreams of that Mallinckrodt salesman who predicted fifteen years ago that aluminum stearate would make a valuable lubricating grease out of a worthless oil. A. T. B.

GENERAL

When two cigarettes are less harmful than one. ANON. *Laboratory*, **9**, 25 (1937).—"Cigarette smokers who inhale from five to ten pounds of nicotine per year and absorb most of the drug into their systems will be interested in the discovery of a method by which as much as eighty per cent. of the nicotine can be removed. The surprisingly simple and efficient absorbent by means of which this is accomplished was recently hit upon by some chemists while making an investigation, the primary object of which was to employ an entirely different material for the purpose.

"Count Giuseppe Cippico, who is connected with a prominent American firm, noted, while abroad, that in Germany silica gel was used as the filtering medium in cigarette holders. He inquired whether activated alumina, well known to laboratory technicians, might give the same or better results, thereby opening a new field of use for that efficient granular adsorbent. American chemists of the Aluminum Company experimented and found that cartridges of the two types of adsorbents extracted practically the same amount of nicotine—about fifteen per cent. This degree of efficiency was not satisfactory. Intrigued by the problem, they conducted more experiments until one day one of the chemists hit upon the idea of trying a cigarette as a filter for the smoke from another cigarette.

"Here he had packed in a neat and convenient form finely divided shreds of tobacco which exposed a large surface area to smoke passed through it, and it did seem that tobacco should be a good absorbent of nicotine. It sounded logical, but surely this was too simple to be the best answer to the problem. Nevertheless, this simple 'filtering cartridge' was tried, and it was found that a fresh cigarette of any commercial brand is the most practical eliminator of the undesirable constituents of tobacco smoke.

"A cigarette used as a filter absorbs its own weight in nicotine and excess tar, yet it does not impart a flat taste to the smoke passed through it. It becomes more absorbent with use and should be discarded only when it is difficult to draw smoke through it—usually after smoking thirty to forty cigarettes. Actual tests show that 30.4 mg. of nicotine are removed from twenty cigarettes when the new filter is used.

"Ebony-finished aluminum cigarette holders have been made which provide a chamber of the proper size and shape to hold a cigarette employed as a filter. A person who smokes a package of cigarettes a day breathes in about 500 mg. of nicotine per week. A fatal dose, taken at one time, is 500 mg. While the human system seems to be able to take care of nicotine if not introduced too rapidly, a dosage which would be toxic if received in the stomach in one-half hour is contained in the smoke of three cigarettes. The unhealthful situation is that smokers almost continually are experiencing a condition near the danger point.

"Because one cigarette acting as a filter for the smoke of another cigarette absorbs about fifty-five per cent. of the total nicotine present, the harmful effects from this source are reduced correspondingly when two cigarettes are used tandem in the new holder.

"It has been aptly said that you may know where a research begins but you never know where it will end." A. T. B.

Table talk. ANON. *Ind. Bull. of Arthur D. Little, Inc.*, **129**, 3–4 (Oct., 1937).—Engineering in the food industries is receiving increased attention, especially along lines which seek to preserve foods almost indefinitely without loss of flavor, taste, or valuable vitamins. Emphasis is being placed on the various "quick-freezing" methods. For example, beef is placed in a latex rubber bag, the air in the bag being removed by a vacuum pump, and the bag is then brought into contact with a frigid brine spray. This process is said to reduce the oxidation of fats to a minimum. "Flash processing" is expected to prevent spoiling of canned foods. The "Stero-Vac" process for treating fruit and vegetable juices features flash heating. "Paraweld," a composition which is tasteless and odorless, flexible, thermoplastic, and waterproof, is an improved packaging material. Parafilm permits such foodstuffs as natural cheese to be put up in attractive, easily identified packages which are moisture-proof and prevent growth of mold. Irradiated Vitamin D milk is regarded by some authorities as the most important development of dairy technology since pasteurization. You may buy your fish in a generous supply of crushed antiseptic ice. Gas storage of chilled beef is now a normal commercial practice. Carbon dioxide and oxygen are the two most important gases used. G. O.

RECENT BOOKS

A LABORATORY MANUAL OF COLLEGE CHEMISTRY. *H. G. Deming*, Ph.D., Professor of Chemistry, University of Nebraska. Fourth edition. John Wiley and Sons, Inc., New York City, 1937. viii + 268 pp. 50 figs. 21 × 27.5 cm. $1.75 net.

This manual is intended for use in an elementary course in general chemistry. It is well put together and bound with a metal spiral, which insures its lying flat on the desk when in use. This, it seems, is of distinct value to the student. The paper is of good grade and the printing clear and precise. The increase in the size of page makes this edition far more readily adaptable to laboratory use than any of the previous editions.

There are sufficient experiments in the manual for only one semester of a course having two two-hour laboratory periods per week. The forty-eight experiments are divided into seven groups, apparently on a more or less arbitrary basis, although the author makes the point in the preface that the "instruction is cumulative, each exercise being based on those that precede....." Each group of experiments is concluded with a so-called laboratory problem which in itself constitutes a review of the preceding group of experiments. It seems to the reviewer that this testing device merits praise.

The experiments are well selected, with a view to making it possible for the college student to perform many experiments which would not be done on the secondary-school level. This will go a long way toward reducing to a minimum that ever-present problem of duplication of secondary-school chemistry during the first year of college work. The insertion of report sheets following each experiment provides a definite means of ascertaining whether or not the student has achieved a thorough understanding of the experiment performed. In the opinion of the reviewer, the descriptive matter accompanying each experimental outline could be advantageously reduced to a considerable extent. As it is, the student must read through a good deal of rather closely printed matter in order to find the essential parts of the experiment.

The author recognizes the principal function of laboratory work, namely, to illustrate the scientific method. However, he maintains there is a need to discard some traditional experiments and break with traditional methods. This he has done both in the selection of experiments and in the arrangement of them.

The latest edition of this manual represents a sincere effort on the part of the author to provide the very best teaching aid possible, and in the opinion of the reviewer he has succeeded very well.

R. K. CARLETON

RHODE ISLAND STATE COLLEGE
KINGSTON, RHODE ISLAND

GENERAL CHEMISTRY EXPERIMENTS. *R. D. Billinger*, Ph.D., and *Hilton A. Smith*, Ph.D., Lehigh University. Rhode Printing and Publishing Co., Kutztown, Pennsylvania. 1937. ix + 281 pp. 27 figs. 15 × 23 cm. $2.25.

This compilation of experiments in general chemistry is presumably designed for the usual freshman college course. The authors address a very brief preface to the student but do not indicate their intentions for the book.

The experiments are written in a descriptive form without divisions such as materials, object, discussion, or procedure. Each exercise is followed by a perforated data and question sheet, which, we assume, is to be filled out during the progress of the laboratory period and left with the instructor. It is not quite clear whether or not the authors require a notebook in addition to this report. At the end of Experiment 8, the student is directed to "record the data in your notebook"; however, in Experiment 14, he is instructed to "sketch your apparatus in your book," which obviously means on the perforated sheet.

The experiments are well selected and quite representative of those usually found in manuals for general chemistry. Among the ones seldom included the following may be mentioned, molecular weight determination of naphthalene by the boiling-point method; a measure of catalysis; dyeing by mordants; fire-proofing paper; mosaic gold; and preparations of pyrophoric lead, ozone, Na_2CO_3 by Solvay, C.P. NaCl; KIO_3, pure Ag, AsH_3, and woods metal. Of the common topics not included in this book the most obvious are Charles' Law; Boyle's Law; hydrolysis; oxygen content of the air; organic compounds other than CH_4 and C_2H_2; conversion of chemical energy to electrical energy; Mg, Ba, Ca, Sr, K, and their compounds.

In spite of the many discussions in the Section of Chemical Education ionic reactions are still classified as "double decomposition" and strong electrolytes are spoken of as having eighty molecules "split up in the form of ions and twenty existing as whole molecules."

The procedures, in general, are in accordance with good technic; however, in illustrating the law of conservation of mass, a 150-ml. flask is used to contain such a small quantity of reactants that the student could not detect a change in weight if any were involved. In the distillation experiment, it would be better to use an all glass condenser instead of a rubber connection.

The book shows faults common to most first editions which do not have the benefit of an experienced editor. Sentence structure may be improved in several places, and locally applicable statements such as "secure from the office window" are found occasionally.

On the whole, the book is assembled in good form, the printing is easy to read, and students should have no difficulty in following the procedures. The inclusion of experiments which have previously been available only in journal form is sufficient to warrant this addition to the list of laboratory manuals.

CHARLES E. WHITE

UNIVERSITY OF MARYLAND
COLLEGE PARK, MARYLAND

LABORATORY MANUAL OF GENERAL CHEMISTRY. *Harry N. Holmes*, Professor of Chemistry in Oberlin College. Fourth edition. The Macmillan Company, New York City, 1937. viii + 299 pp. 31 figs. 21 × 26.5 cm. $1.50.

Professor Holmes' books are always interesting, no matter what the style in which they may be cast. The fourth edition of this laboratory manual contains essentially the same experiments as the third, but the physical appearance is very different. The page size is larger, the unprinted pages for students' notes have given way to blank spaces after each question, and the leaves are perforated so they can be removed from the book for the teacher's examination. The use of two metal rings makes it possible to return these leaves to their places.

The manual contains one hundred thirty-six experiments, some of which are rather long, so that a class could not expect to complete all of them in a one-year course. Asterisks indicate fourteen complete experiments and parts of nineteen others which may be reserved for the better students. There are nineteen quantitative experiments, all of them in the first half of the book. It is interesting to note the large number of references to the JOURNAL OF CHEMICAL EDUCATION.

Experiments not included in the previous edition are the Determination of the Atomic Weight of Tin; the Freezing Point Lowering of Camphor and Menthol; the Determination of pH Values by Indicators, and Double Salts, Complex Salts and

Solid Solutions. The Determination of the Formula of Silver Iodide, the Determination of the Molecular Weight of Ether, and the Catalytic Preparation of Hydrogen Iodide are new experiments which have been developed by the author and his students. Some of the less satisfactory experiments of previous editions have been omitted. While most of the assignments can be performed with apparatus and materials readily available, a few are quite complicated, and some require apparatus not usually available to elementary students. The large number of experiments, however, makes a wide choice possible.

Experiments bearing on theoretical problems are preceded by lucid discussions of the principles involved. The questions accompanying the experiments are particularly well done, and should sharpen the student's powers of observation and encourage clear thinking. The appendix (seven pages) should prove useful both to student and teacher.

This book is certainly one of the better current laboratory manuals. Conservative in approach, it is yet readable and stimulating, and is a splendid companion to Professor Holmes' GENERAL CHEMISTRY and INTRODUCTORY CHEMISTRY.

JOHN C. BAILAR, JR.

UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

AN OUTLINE OF ORGANIC CHEMISTRY. *Ed. F. Degering*, Assistant Professor of Chemistry at Purdue University; *R. E. Nelson*, late Professor of Organic Chemistry at Purdue University; *J. R. Harrod*, Professor of Chemistry at Ohio Northern University, and others. Barnes and Noble, New York City, 1937. xvi + 317 pp. 13 × 21 cm. $1.25.

This outline, in addition to the authors mentioned above, bears the names of seventy-seven assistant editors from almost as many universities, colleges, and industries. In spite of the large number of collaborators there seems to be no lack of uniformity in the presentation of the material. As the name indicates, the book is in outline form and, except in the special chapters, most of the information is given by equations with further discussion only in exceptional or unusually important cases. The relative importance of the material has been indicated by the use of different sizes of type.

After the usual introductory material there is a chapter on the electronic basis of valence. This is followed by one hundred thirty pages devoted to aliphatic chemistry, three to alicyclic, forty-six to aromatic, and four to heterocyclic compounds. There are additional chapters on foods and metabolism; non-metallic and metallic alkyl derivatives; miscellaneous compounds; pronunciation and nomenclature; antiseptics and germicides; dyes, stains, and indicators; terpenes and rubber; synthetic resins; isomerism; and a summary of "named" reactions, processes, syntheses, and tests. Most of these special chapters and the section on carbohydrates are especially well done, although the material on dyes and on carbohydrates seems rather comprehensive in comparison to the rest of the book. The inclusion of a chapter on pronunciation and nomenclature is an idea that is worthy of general adoption by authors.

The chapter on "named" reactions seems to have been carried to extremes. It contains one hundred sixty-nine processes, syntheses, or tests, including the following: Ciamician-Dennstedt synthesis, Crum-Brown and Walker reaction, Diels-Wolf reaction, Engler-Weissberg hypothesis, Freund reaction, Gladstone reaction, Komppa synthesis, Prileschaiev reaction, Schorigin reaction, Walker reaction, Wohl-Schweitzer electrolysis, and Wislicenus synthesis. These are reactions that are generally familiar to organic chemists, but it is doubtful if the majority of experienced organic teachers would recognize all of them by their names.

While the chapter on electronic structure is well done, it is ignored in the rest of the book; in fact, the next chapter begins with the explanation that hydrogen and carbon have valences of one and four, respectively. No mention is made in the body of the book of the structure of oxidized sulfur compounds or of amine salts.

The continued use of such names as ethanoic acid, sodium ethanoate, ethyl ethanoate, and ethanenitrile does not seem wise, since these are not the names the student will find in the literature. It would seem better to accept the index of *Chemical Abstracts* as a guide for practical usage.

The book is quite free from misprints, but several errors of facts were noted. Noteworthy among these is the mechanism of the Skraup synthesis and the structure of the products formed by the reaction of mercaptans with olefins. Time will probably make correct the statement that acetic acid is made commercially from carbon monoxide and methanol. The omission of copper from the equation for the preparation of phenol from chlorobenzene and the failure to show acetal formation as reversible might be considered as errors. The manner in which rectangles are drawn to indicate the elimination of water, halogen acids, and other simple substances may lead to incorrect conclusions on the part of the student; for example, this gives an improbable mechanism for the Fittig-Erdman synthesis and it might be inferred that aldehydes are formed by the hydrogenation of acids and esters, that the reaction of sodium bisulfite with ketones is general, and that the aldehyde ammonias are simple addition compounds. The presence of a catalyst is often indicated in cases where the specific nature of the catalyst might be mentioned.

The stated purpose of the outline is to replace "prolific" [*sic*] lecture notes rather than as a substitute for a text. It is probably unjust for one who has had no experience with the book to attempt to evaluate its success from this standpoint. While the reviewer is unconvinced that this would be an improvement upon the customary lecture system, the number and character of the assistant editors indicate that it does serve the purpose in many courses. In addition, students in courses which are not based on the outline will find it valuable for review, especially if their lecture material has been poorly organized.

RALPH CONNOR

UNIVERSITY OF PENNSYLVANIA
PHILADELPHIA, PENNSYLVANIA

THERMODYNAMIC THEORY OF AFFINITY: A Book of Principles. *Th. De Donder* and *Pierre Van Rysselberghe*, Stanford University. Stanford University Press, Stanford University, California, 1936. xx + 142 pp. 16 × 24.5 cm. $3.00.

The objectives and methods of this brief treatise are very different from those of familiar thermodynamical texts. Superficially it bears considerable resemblance to them, for many of its equations are formally similar to those of conventional thermodynamics. The meanings of the symbols in some of the most important of these equations, however, are quite different from the familiar ones. The usual basis for applications of the second law of thermodynamics is the following equation relating the heat absorbed in a *reversible* process to the temperature and entropy

$$dQ - T\,dS = 0$$

De Donder and Van Rysselberghe are concerned with the heat absorbed in *irreversible* chemical changes which is given by

$$dQ - T\,dS = dQ'$$

where dQ' is the so-called uncompensated heat of the *irreversible* transformation.

It is claimed that De Donder's methods are applicable to such problems as reaction velocities, statistical theories of physical chemistry, overvoltage phenomena, etc. Numerous papers on such subjects have already appeared and the authors plan to contribute, in the near future, several books dealing with these and similar subjects.

Dr. Van Rysselberghe has rendered a service to physical chemists in presenting this convenient summary of numerous papers on De Donder's methods. The coming books will be awaited with

interest by the readers of this one. It is to be hoped, however, that the new volumes will contain much more discussion of the validity of some of the fundamental equations, and of the significance of some of the newly defined variables. Final judgment of the whole method of attack will depend not only upon its success in correlating experimental facts but also upon adequate justification of the equations, some of which are presented in this Book of Principles without proof and with but little argument. This first book is not in itself either complete or convincing.

T. F. YOUNG

UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS

GENERAL CHEMISTRY FOR COLLEGES (REVISED). *B. Smith Hopkins*, Professor of Inorganic Chemistry in the University of Illinois. D. C. Heath and Company, Boston, 1937. 758 pp. 58 tables. 264 figs. 15 × 22.3 cm. $3.72 (List Price).

LABORATORY EXERCISES AND PROBLEMS IN GENERAL CHEMISTRY. *B. Smith Hopkins*, Professor of Chemistry, University of Illinois, and *M. J. Copley*, Assistant Professor of Chemistry, University of Illinois. Third edition. D. C. Heath and Company, Boston, 1937. 243 pp. 29 figs. 16.5 × 24 cm. $1.76 (List Price).

The new edition of this well-known text has been thoroughly revised, both in organization and content. The treatment of atomic structure has been moved up to the second chapter, and this is followed immediately by a discussion of the periodic table. In the preface the author states, "The great advantage of this order of presentation is that it furnishes a more logical and more comprehendible approach to the difficult subject of valence."

A new chapter has been added on electrochemistry. The theory of solutions is presented from the modern point of view but in non-mathematical form. New topics, new illustrations, and new references are used throughout to modernize the text. Dr. Hopkins makes the significant observation, "It is still evident that the first essential in teaching chemistry is to create interest."

In this third edition of the LABORATORY EXERCISES there are one hundred nine experiments under parts one and two, and one hundred fifty problems under the section headed "Chemical Arithmetic." The binding of the laboratory manual permits the ready removal of the blank pages on which the student records his observations. Both the text and the manual show the careful attention to detail that is characteristic of Dr. Hopkins' teaching.

JOHN R. SAMPEY

FURMAN UNIVERSITY
GREENVILLE, SOUTH CAROLINA

THE CHEMISTRY OF RUBBER. *H. Freundlich*. The Chemical Publishing Company, New York City, 1936. xi + 72 pp. 10 × 16.5 cm. $1.25.

The name is entirely too short for such a little book. The title would be more descriptive of the contents if it were "Some Problems in the Colloidal Chemistry of Rubber." The book is not critical. It merely sets forth observations by various investigators and the deductions drawn therefrom. Where there are differences of opinion, both sides of the controversy are treated impartially.

The colloidal problems of rubber latex are treated separately from those of coagulated rubber, as, of course, they should be. This appears to be the best section of the book. The X-ray studies of rubber are reviewed, as is the Joule effect in comparative detail.

A third section of the book is devoted to botany and history of rubber. It is distressingly short.

The book would certainly be of interest and value to high-school students as an accessory to general reading in the field of chemistry, but scarcely as a text, since organic chemical considerations and technological practices are almost completely absent. The data is far from up-to-date or novel and in some cases slightly inaccurate. The following two sentences under the heading "Some Historical Remarks" will exemplify this last statement. "When America was discovered by the Spaniards they found the natives using primitive rubber articles, balls, shoes, etc. The natives even seem to have succeeded in vulcanizing them, by adding occasionally sulphur or gunpowder to the latex." I wonder where the natives obtained their gunpowder before the Spanish discovered America.

THOMAS MIDGLEY, JR.

ETHYL GASOLINE CORPORATION
WORTHINGTON, OHIO

HENLEY'S TWENTIETH CENTURY BOOK OF TEN THOUSAND FORMULAS, PROCESSES AND TRADE SECRETS. Edited by *Gardner D. Hiscox*, M.E. 1937 Revised and Enlarged Edition by *Prof. T. O'Connor Sloane*, Ph.D. The Norman W. Henley Publishing Company, New York City. ii + 923 pp. 14 × 22 cm. $4.00.

This handy reference work is too well known to require detailed description. For many years HENLEY'S TWENTIETH CENTURY FORMULA BOOK has been a standard book of formulas, processes, and recipes. It is intended for the use of anyone having the remotest connection with a laboratory, workshop, or kitchen. More than ten thousand formulas are offered.

The new edition is the ninth revision, and much new material has been added. New special features are a classified buyer's guide, and a glossary of chemical terms with their corresponding common names.

Many chapters of the book have been enlarged and thoroughly revised to bring them up to date. This is particularly true of the sections on Adhesives, Cosmetics, Lacquers, Paints, Photography, and Polishes.

Numerous formulas and processes of questionable merit of the previous edition have been discarded. However, it is the humble opinion of the reviewer that the editor did not go quite far enough in this direction, as some obviously obsolete and useless material has unfortunately escaped his surveillance. The few pages on Pyrotechnic Magic should unquestionably be omitted in the interest of human safety. Biting off a piece of red-hot iron by "grasping the broken end in your teeth, being careful not to let it touch your lips or tongue," or lowering a flaming candle wick saturated with kerosene in the mouth, "while exhaling the breath freely," seems like a sure fire method of obtaining major injuries for anyone sufficiently foolhardy or gullible to attempt these "miracle" effects.

Despite these objections, the book contains enough valuable data to make it a worth-while addition to any laboratory or work shop.

M. H. DASKAIS

5456 UNIVERSITY AVENUE
CHICAGO, ILLINOIS

LABORATORY MANUAL IN CHEMISTRY. *R. E. Horton*, Seward Park High School, New York City. D. C. Heath and Company, New York City, 1937. xi + 99 pp. 42 figs. 14 × 20.5 cm. $1.00.

In his preface the author states he is providing, by demonstrations and individual laboratory exercises, a program of activities which will teach the understanding of chemical principles through the observation of facts, and at the same time give training in scientific methods.

The book contains introductory exercises in the use of laboratory equipment and in glass working, followed by one hundred thirty-one experiments and fifty-five projects. The experiments and projects cover a wide field of information and give opportunity to learn much laboratory technic. They are conveniently grouped into a set of general tests, tests for food preservatives and adulterants, cleaning and sanitation, study of textiles, inks, and dyes, and some chemical processes and products of daily life.

The directions are in general clear and concise. Occasionally one meets vagueness, which should not be found in high-school experiments as, "Heat some copper turnings with some moder-

ately dilute nitric acid." "Some" and "some moderately dilute" are too indefinite. In another experiment one reads, "Distill a mixture of sulphuric acid and sodium nitrate in a glass retort." Some experiments tell the student to use teaspoons of material. Would it not be better to give the amounts in the more scientific terms of cubic centimeters? The experiment on proximate analysis of coal starts out to get the per cent. of ash but gives no directions for so doing. As given the coke and ash are considered all coke. Sometimes the statement of the problem is too verbose as, "What are the products of heating mercuric oxide in a hard glass test-tube?" Would there be different products of decomposition if different apparatus is used? Poor phrasing is sometimes encountered as, "Make the experiment—," "Make the electrolysis of water."

Almost every experiment is followed by questions or incomplete sentences. These often defeat the learning of a scientific method as they cannot be answered from the data obtained from the experiment. Instead of making accurate conclusions from his own observations the beginning student would have to copy his information from some text. Perhaps the author intends this as he often gives definite references to his own book, MODERN EVERYDAY CHEMISTRY. Laboratory work should teach a student to observe, and then he should learn the difference between what he sees (data obtained) and what he thinks about it (conclusion) and be able to write it without suggestive questions. Class discussion should tie up the laboratory work with the reading.

The experiments are short enough—most of them—to be completed in the hour period now given to science in many high schools. Teachers will find in them much suggestive material that can be used with any text.

HATTIE D. F. HAUB

ROOSEVELT HIGH SCHOOL
OAKLAND, CALIFORNIA

LABORATORY PRACTICE OF FIRST YEAR COLLEGE CHEMISTRY. *G. N. Quam*, Associate Professor of Chemistry, Long Island University. Edwards Brothers, Inc., Ann Arbor, Michigan, 1937. v + 94 pp. 38 figs. 21.5 × 27.5 cm. $1.75.

Throughout the forty-eight exercises contained in this manual, the author has made significance the first consideration. Seventeen involve quantitative determinations and seven may optionally be given by lecture demonstration, the calculation of results being assigned to each student.

A number of unusual experiments involving catalysis, reaction velocity, colorimetry, molecular weight determination, the law of multiple proportions, the colloidal state, and other topics, offer opportunity to impress fundamental chemical phenomena strongly upon competent students. Practical exercises involving purification of materials, volumetric determinations, and water softening are offered. Qualitative analysis is introduced in connection with observations of important properties of chosen elements. Microchemical tests by drop reactions are used in several exercises in inorganic preparations. The student's grasp of experiments is frequently checked by means of unknowns. The use of a number of good references, rather than one text is encouraged.

The material offered is sufficient and important, and should be distinctly of aid to the conscientious teacher in giving his students a firm foundation of chemical fundamentals.

LOTHROP SMITH

THE STATE UNIVERSITY OF IOWA
IOWA CITY, IOWA

ELEMENTARY CHEMISTRY, with Practical Applications. *Imo P. Baughman*, Ph.D., Instructor in Chemistry in the Los Angeles Junior College, Los Angeles, California. Second edition, revised. Lea & Febiger, Philadelphia, 1937. 296 pp. 19 figs. 13 × 20 cm. $2.75 net.

This text is designed to be especially useful to the student who is preparing to become a trained nurse. It would also serve the future dietitian. The author considers that in addition it affords a good account of chemistry for the general student who may find it of value in home making. The implication in the subtitle is that the emphasis is on practical applications of chemistry.

To these ends the author does not neglect to cite many applications of each of the topics that he teaches. The book is full of useful information about things chemical. The medical slant frequently appears, as, for example, when acids and bases are taught, the subject of acid and basic "burns," and their treatment follows.

The bare fundamentals of general chemistry are covered in the first four parts of the text (one hundred sixty pages) and then comes a somewhat extended treatment of carbon compounds, a section on "Foods and Digestion" with units on fats, carbohydrates, proteins, vitamins and minerals, and enzymes. A part on "Body Fluids" treats especially of "Blood" and "Urine." The final part deals with "Textiles" and "Cleaning of Materials."

A brief study of some parts of the teaching of fundamentals shows that much "telling" is necessary to cover the necessary ground in such small compass. The tale is well told, as a rule; for example, the exposition of the subject of pH is excellent, and many a "chemist" who makes his living by making pH determinations might study it to advantage to clarify his thinking about what he is up to. To an educator who has the time to develop the laws and theories of chemistry, with their biographical and historical background, and with suitable use of original sources, the rapid fire treatment, with its very sketchy outlines, is almost painful. Necessity, however, rather than inclination, doubtless forces this method of teaching on those who must speedily prepare special students.

FRANK B. WADE

SHORTRIDGE HIGH SCHOOL
INDIANAPOLIS, INDIANA

CHEMCRAFT EXPERIMENT BOOK. *Harold M. Porter* and *Jermain D. Porter*. The Porter Chemical Co., Hagerstown, Maryland, 1937. 237 pp. Numerous illustrations. 12.5 × 20.5 cm. $1.50.

This manual is an instruction book intended to accompany the "Chemcraft" outfits, of which so many thousands have been sold to "Young America." It cannot be denied that much interest in chemistry has been aroused through the efforts of the Porter Chemical Company to enlist the youth of this country in a great army of chemical experimenters. While much of this activity has been play, numerous youngsters have told the reviewer that their subsequent election of chemistry as a serious study resulted from the interest aroused through the possession of a "Chemcraft" set.

The EXPERIMENT BOOK gives, in a well-organized manner, a very extensive course in laboratory chemistry, but one calling for a minimum of equipment. The units remind one of an up-to-date textbook in their content and order: Elements; Acids-Bases; Indicators; Physical Forms of Water; Nitrogen; Hydrogen; Water; Surface Tension; Solutions, etc.; in the earlier part of the book and then much descriptive chemistry, followed by such units as Fuels; Metallurgy; Glass; Paints; Lacquers and Varnishes; The Dyeing Industry; Perfumes; Adhesives; Photography; Leather; Paper; Foods; Agricultural Chemistry, and finally, in Part II, Chemical Magic. Eight hundred fourteen experiments are provided.

The directions are clear and concise and care is taken to avoid dangerous situations and to caution against accidents. Much interesting information, most of it correct, is provided in the introductions to the several units.

Educators may well take serious notice of the method and results of this really successful EXPERIMENT BOOK.

FRANK B. WADE

SHORTRIDGE HIGH SCHOOL
INDIANAPOLIS, INDIANA

ANALYSES BY SPOT TESTS

. . . Convenient for rapid qualitative determinations

. . . Require only small amounts of unknown and reagent

. . . Specific for the compound under test

THE PROVED VALUE of spot tests justifies their inclusion in the analytical course.

The Eastman reagents for spot tests—more than 75 of them—now are supplied in 1- and 5-gram bottles. A special list of these compounds, reprinted from *Eastman Organic Chemicals*, List No. 28, will be forwarded upon request. . . . Eastman Kodak Company, *Chemical Sales Division*, Rochester, N. Y.

EASTMAN ORGANIC CHEMICALS

WERTHEIM—Laboratory Guide for Organic Chemistry

This book presents experimental material for a year's course in elementary organic chemistry. It is especially designed for students majoring in chemistry or following the engineering or premedical curriculum. 24 Illustrations. 524 Pages. Heavy Paper Covers $2.00

By E. Wertheim, Ph.D., Professor of Organic Chemistry, University of Arkansas.

HACKH—Chemical Dictionary, 2nd Edition

This work has been completely revised and reset to incorporate the new material. Nearly 10,000 new definitions, 230 more pages of material, about 100 new and original tables, 477 short biographies of chemists, new illustrations, new diagrams, etc., have been added. 1020 Pages. About 50,000 Terms pronounced and defined. Washable Covers $12.00

By Ingo W. D. Hackh, M.A., F.A.I.C., F.R.S.A., Prof. of Chemistry, College of Physicians and Surgeons (San Francisco, Calif.) Author of "Chemical Reactions and Their Equations," "Structure Symbols of Organic Chemistry," etc.

MULDOON—Textbook of Organic Chemistry

For Students of the Medical Sciences. 2nd Ed.

This textbook presents material for an interesting and modern full year's course in organic chemistry for beginners. It is designed for those preparing for medicine, pharmacy, dentistry, etc. 33 Illustrations, 590 Pages. Washable Cloth $3.00

By Hugh C. Muldoon, D.Sc. (Duquesne University)

POPOFF—Quantitative Analysis. 3rd Edition

This book presents material for a short course in elementary and also in advanced quantitative analysis. 75 Illustrations. 555 Pages. Cloth $4.00

By S. Popoff, Ph.D., Revised by M. J. Rice, Ph.D. and W. P. Cortelyou, B.S., Alfred University

P. BLAKISTON'S SON & CO., Inc. 1012 Walnut Street, Philadelphia, Pa.

TRADE ANNOUNCEMENTS

Cameron pH Meter

The Cameron pH Meter, distributed by *Wilkins-Anderson Company, 111 North Canal Street, Chicago, Illinois,* is a most versatile instrument, using any glass electrode. It reads directly in pH figures, and no calculations are necessary. For oxidation-reduction work, a double-scale model is available which reads in pH and also directly in millivolts. While it is not a field instrument, it may be carried about easily.

Sustained accuracy most necessary for plant or research work is a feature. The *Cameron* is, therefore, designed for greater deliverable accuracy in the laboratory and for sturdy service in factory control work. The "A" batteries, regularly supplied, should, therefore, be replaced by a small storage battery and trickle charger. Our experience in hundreds of installations indicates that self-contained instruments are operated much below their rated sensitivity and accuracy, because the "A" batteries are operated below their full charge.

Important, too, the *Cameron* calibrating adjustment is such that any commercial glass electrode or laboratory blown glass electrode may be used, whether the Ag-AgCl platinum-quinhydrone or other inner system is used. Even the antimony stick electrode may be substituted for the glass electrode and readings made directly in pH units. The *Cameron* glass electrode has a heavy outer wall, protecting perfectly the pH glass on the inside. The inner system is the usual lead-lead chloride, refillable type, the solution being replaced about every three weeks or so.

Stopcock Greases

Greases made for use on glass cocks in vacuum lines have been developed by the *Westinghouse Electric & Manufacturing Company* because no lubricants satisfactory for this purpose were available. Four types of grease are announced.

Stopcock grease Number 6 is for vacuum line stopcocks which may be subject to high temperatures. It is very viscous even at relatively high temperatures.

Number 7 is for glass stopcocks in high vacuum exhaust systems. It will not readily release gases which would interfere with vacuum readings.

Number 8 is for the lubrication of rubber hose connections to metal tips of vacuum exhaust pumps. Not only will it lubricate such a joint, but it will also assist in making it vacuum tight.

Number 10 is recommended for general laboratory use. Its light consistency makes it most suitable for atmospheric pressure use and for easier manipulation during the winter months. It is particularly adapted to desiccator use.

New Thermionic Amplifier

Bringing high sensitivity to potential measurements in high resistance circuits, this Thermionic Amplifier, manufactured by *Leeds & Northrup Company, 4901 Stenton Avenue, Philadelphia,* drawing a negligible current, adapts any potentiometer of suitable range to the measurement of glass electrode potentials. It is also useful for measuring potentials encountered in polarization studies. In this application it is possible to supply a limited polarizing current of controlled direction and magnitude while actually measuring potential. Other uses include the measurement of corrosion and oxidation-reduction potentials. Resistors of high values can be measured at voltages at which they are used. Other applications, involving precise measurement of potential or current in circuits of extremely high resistance, will be apparent to many users.

Simple and easy to operate, it requires little manipulation other than preliminary adjustments. Readings are rapidly obtained by the routine potentiometer measurement. Built with typical *L&N* thoroughness of detail in design and construction, this is a particularly versatile instrument for which many uses may be found in the laboratory.

Weston Equipment Bulletin

"Weston Test Equipment For Industry, School and Laboratory," a new bulletin describing multi-range test equipment of high flexibility, has just been issued by the *Weston Electrical Instrument Corporation, Newark, N. J.* This bulletin illustrates six standard models of the multi-range test instruments, and contains complete descriptions of their uses, ranges, electrical specifications, dimensions, and prices.

Among the instruments discussed are the Type 1 analyzer (volt-ohm-milliammeter), which measures A.C. and D.C. voltage, direct current and resistance over a total of thirty-three ranges, all contained in this one instrument and also the multi-range ohmmeter, for resistance measurements from 1 ohm to 300 megohms on six scale ranges. Other instruments discussed are the capacity meter, the volt-ohmmeter, the vacuum tube voltmeter, and the test oscillator.

"Chemcraft" Chemistry Outfits

"Chemcraft" Chemistry Outfits, manufactured by the *Porter Chemical Company, Hagerstown, Maryland,* are a source of pleasure and instruction to many children who are interested in science.

The problem of maintaining high quality in the materials used in "Chemcraft" sets is given much more serious attention than in the average toy. Instructions must be kept up to date and must be accurate, as well as simplified for young minds. Materials must be of the best quality available.

The *Porter Chemical Company* uses Kimble Glassware in all "Chemcraft" sets, because of the uniform quality, excellent workmanship, and accuracy of Kimble Laboratory Glassware.

"Avitex"

A new textile finish assistant is announced by the *du Pont Company* in "Avitex" M (Patented), a specially sulfated fatty alcohol recently developed. It is designed primarily as a softening agent for use with high concentrations of epsom salts, such as are employed in the preparation of heavily weighted finishes where the stiffening effect of starch products or minerals is to be avoided. The new product forms clear, stable emulsions, in the presence of epsom salts, which show no separation on prolonged heating, thus eliminating formation of oil spots on fabrics and loss of material from the bath.

New Neutral Wedge Photometer

The new Aminco Neutral Wedge Photometer, an outgrowth of apparatus developed in the laboratories of the Food & Drug Administration of the U. S. Dept. of Agriculture, is announced by the *American Instrument Company, Silver Spring, Maryland.*

This type of instrument has been used extensively there and elsewhere for the precise determination of micro and macro quantities of lead, fluorine, arsenic, lactic acid, iron, indole carotene, chlorophyll, xanthophyll, phosphorus, vanadium, titanium, lactoflavin, organic spray residues such as nicotine and phenothiozine, and for determining the extent of damage to wool fibers. It can also be used for many other substances and for practically all clinical determinations using color reactions, such as blood and urine analyses, turbidimetric measurements, and color control work with oils, beverages, etc. Complete details are contained in the manufacturer's Bulletin No. 1025 CE, which is available on request.